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SEMI-ANNUAL REPORT

OF

SCHIMMEL & Co.

(FRITZSCHE BROTHERS)

MILTITZ

NEAR LEIPZIG

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APRIL/MAY 1906.

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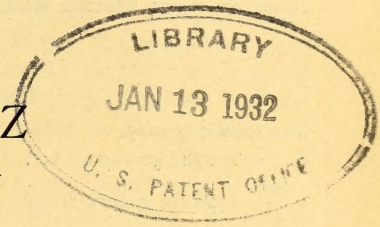

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List of abbreviations.

d = specific gravity.

d_{200} = specific gravity at 20°.

$d\,\frac{20^\circ}{4^\circ}$ = specific gravity at 20°, compared with water at 4°.

$\alpha_{D\,15^\circ}$ = optical rotation at 15°, in a 100 mm. tube.

$[\alpha]_D$ = specific rotation.

$n_{D\,15^\circ}$ = index of refraction at 15°.

n = normal.

$\frac{n}{2}\left(\frac{n}{10}\right)$ = semi-normal or deci-normal (titrated solutions).

gm. = gram; cc. = cubic centimeter; mm. = millimeter.

Temperatures are uniformly stated in **centigrade** degrees (°).

Miltitz, near Leipzig, April/May 1906.

In looking back on the year 1905, we can rejoice in the fact that the economic situation of Germany shows a further favourable development. The industrial activity was in part exceptionally animated, having largely recourse to the money market, — although the surprising increase of the bank-rate at the close of the year, as compared with the low rates at other of the world's principal exchanges, may perhaps have been due, not so much to a healthy development of industry, as to important financial engagements on the exchange, and speculative purchases of goods in view of the increases in the import-duties about to come into force. This state of extreme exertion gives food for thought, and may possibly lead to an increase in the resources of the Imperial Bank.

The new Tariffs naturally claimed the largest amount of interest. Since these Tariffs have become an established fact, each individual branch of industry will have to make for itself the best of the bargain.

In our own branch, the alterations are not of any very considerable importance. It is to be appreciated (because it adds to our capacity of competing with foreign countries), that after struggles lasting for many years, seeds for the production of essential oils are now at last to be admitted free, subject to official control, and the distillation-residues are likewise to be free, whilst at the same time the import-duty of these materials, in so far as they are used for other purposes, is raised from 3 to 4 marks per 100 kilos.

The duty on essential oils imported from Tariff countries (such as Italy, Russia, Bulgaria) has remained as hitherto at 20 marks, but for the other countries has been raised to 30 marks.

Vanillin, which up to now paid 50 marks duty, has been raised to 80 marks; oils of rosemary and juniper-berries have been advanced from 12 to 30 marks per 100 kilos. On the other hand, oils of turpentine, pine-needles, camphor, and juniper-tar *(ol. cadin.)* remain as before free of duty. We will return to the details when discussing the individual articles in the following pages.

In spite of the internal disturbances in Russia, our trade with that country was unusually brisk, to which the various alterations in the tariff also contributed. The importance of this market for our

products is clear from the fact that the total imports of essential oils in 1903 amounted to:

5436 poods, value 580984 roubles,
33 „ rose oil, value 83295 roubles,

of which from Germany:

2914 poods, value 312531 roubles,
10 „ rose oil, value 30260 roubles.

The principal alterations in the Russian tariff, which came into force on 1st March, are: essential oils, hitherto 24,— roubles plus 10%, now 26,40 roubles, according to treaty 16,80 roubles. Essences and fruit-ethers, hitherto 10,80 roubles, in future 25,— roubles, in bottles 30,— roubles. Extracts and pomades below 10 pounds from 13,60 to 52,50 roubles, according to treaty 36,75 roubles. Pomades in vessels containing at least 10 pounds, according to treaty 15,— roubles per pood gross. Vanillin, coumarin, heliotropin, from 2,25 to 24,— roubles, according to treaty 16,80 roubles. Nitrobenzene from 2,25 to 4,— roubles; menthol, thymol and similar chemical products not specially enumerated from 2,25 to 5,— roubles, according to treaty 4,— roubles per pood gross.

A unique case in the matter of tariffs is no doubt this, that according to the new treaty with Bulgaria, the import duty on essential oils, fruit-essences, and ethers, has been raised to 500 francs per 100 kilos, whilst Germany has agreed by treaty to a reduced tariff rate of 20 marks per 100 kilos for the importation of Bulgarian rose oil! The German Plenipotentiary has rendered a bad service to our Industry by agreeing to this.

The statistics for Austria show the following figures: —

Essential oils, imports in 1904:

124445 kilos, value 1700000 krones;

Essential oils, exports in 1904:

73300 kilos, value 573550 krones.

The alterations in the Tariff, as far as our specialities are concerned, are throughout unimportant, and are more for the purpose of rounding off. The oils of which the import duties were raised are Austrian products, and are of no importance for Germany.

The new tariff of Switzerland also brings but few important alterations. The import duty on camphor oil has been reduced from 2 to 1 franc. Safrol, which usually pays 45 francs, is admitted at 10 francs per 100 kilos on production of proof that it is to be used for the manufacture of heliotropin. Some essential oils, such as clove, lavender, spike, juniper, anise, lemon, peppermint, and cinnamon oils,

and further thymol, eucalyptol, and menthol, have been reduced to 8 francs per 100 kilos, whilst the remaining essential oils, in accordance with the treaty, are taxed as hitherto with 45 francs.

The sale of our products in the United Kingdom is growing, and the best possible relations with this important market have been maintained with the help of our London branch.

The imports of essential oils in the United Kingdom were in 1904:

1834421 lbs., value £ 265922,—,

of which from Germany:

107044 lbs., value £ 13824,—,

whilst the exports amounted to

602843 lbs., value £ 83339,—,

of which to Germany:

220922 lbs., value £ 28866,—.

The trade with the United States of North America was very brisk, in harmony with the economic growth of that country. In view of the equality of the mutual interests, it may confidently be expected that the tariff-difficulties, which have arisen may, be removed amicably while the provisional arrangement is in force, and that the result of the negotiations will be a treaty which will satisfy both parties and will be of long duration.

In spite of the critical situation in Japan, our commercial intercourse with that country was more animated than ever. It may be assumed that the new commercial treaty between Japan and China will also increase the purchasing power of the former country.

Of the South American states, Brazil still continues to suffer from the injurious effect of the fluctuating value of the exchange. The efforts made by the Government to bring about stability in the rate of exchange, must be looked upon as having failed. It is evident that the present state of affairs is not calculated to promote commercial intercourse. The prospects in the Argentine Republic are favourable; with a large increase in the immigration, this country is opened up more and more for civilisation, and its internal wealth also finds expression in the low rate of interest.

In Chile it has not yet been possible to carry out the intended introduction of the gold standard. The abundance of ready money, created by large issues of paper, has led to wild speculations, the rapid collapse of which has made numerous victims. Under these conditions a healthy increase in the exports to Chile is unfortunately out of the question.

The continued improvement in the economic situation in Spain finds expression in the uninterrupted rise of the exchange. In the opinion of leading interested parties, the premium on gold may possibly go back still further within the near future. The reform of the alcohol-law, which was almost hourly expected in the middle of December of last year, has been pushed in the background by other questions, and is now entirely in abeyance. The stormy manifestations of protest against this hated law, which in the course of a few months has totally ruined the wine-producers and the alcohol- and brandy-industries, have gradually died away, and the alcohol-question, which is of such importance for the whole country, has been postponed indefinitely.

Trade with France was very brisk on both sides. There can be no doubt that the negotiations at Algeciras having been concluded in a friendly spirit, in spite of a mischief-making press, they will form the basis of mutually satisfactory relations between France and Germany.

The intercourse with Italy was fairly lively. The favourable exchange has made this country a very desirable market.

The past six months show a preponderance of advancing quotations, which have also assisted in bringing about great animation in the trade during the first trimester of the current year, and which open up favourable prospects for the further course of 1906. The internal situation of our branch of industry is unchanged, and strict control is constantly required to prevent the honest trade from being strangled by corruption. In the following pages we endeavour, as usual, to deal with everything worth mentioning from a scientific and commercial point of view, and we hereby express the wish that it may be of interest and advantage to a number of our readers.

Commercial notes and scientific information on essential oils.

Almond Oil, from apricot kernels. The prices of Syrian kernels, which at the commencement of last harvest cost 64 francs, advanced a few francs in the course of the winter, and have kept at that level in consequence of a brisk demand. The selling prices of essential oil were firm, as the production was scarcely able to keep pace with the demand; the sale of pressed oil, however, was slow, at depressed prices. The use of almond oil for cosmetics (cold cream, etc.) appears to have fallen off, owing to the large number of vaseline and lanoline products; the competition of adulterated oils,

which are offered at incredible prices, also renders the sale of the genuine article more difficult.

Almond Oil, pressed from sweet almonds. Our quotations were adjusted in the late autumn in accordance with the cost-price of best quality 1905 Sicilian fruit. There are no grounds for any alteration in these quotations.

Anise Oil. The value of this important article has undergone further improvement since the date of our last Report, and it is probable that it will at least keep at its present level until the new anise-harvest. The same applies to anethol, the use of which for evident reasons is constantly acquiring larger dimensions. We carry on the manufacture of this product (which we were the first to introduce into commerce) on the largest scale, and in respect of quality supply the best that can possibly be attained, but we have been able to prove by numerous examinations, that inferior products are met with in commerce.

According to information received by us direct, a French firm in Bulgaria, which up to the present occupied itself exclusively with the distillation of rose oil, has now also taken up the distillation of Bulgarian anise, and hopes to produce this year a quantity of from 15000 to 20000 kilos anise oil. If this report is confirmed, a new competitor for Russia would here make his appearance.

The favour granted to our industry, to distil anise free from duty, will enable us in future to work up the various kinds of anise with advantage.

The German import of anise in the year 1904 was: —

in Stettin	from	European Turkey	985000 kilos
	„	the Netherlands	257000 „
	„	Russia	36000 „
	„	the German Customs Union[1])	20000 „
		Total	1298000 kilos
in Hamburg	from	the Russian Baltic ports	170600 kilos
	„	Spain	21600 „
	„	Turkey	112100 „
		Total	304300 kilos.

Owing to the unfavourable state of the harvest, the import of anise in 1905 has declined considerably, for example, in Stettin it came to only 196000 kilos; the figures of the import in Hamburg in 1905 have not yet come to hand.

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[1]) Comprising the German Empire and the Grand Duchy of Luxembourg.

Basil Oil. The sources of this preparation which existed up to the present (France and Réunion) have recently become completely exhausted, and only inferior qualities are now met with in commerce. But it may be assumed that this scarcity will be relieved in the course of this summer. If the weather-conditions are favourable, we hope to produce some of this oil ourselves.

Oil of Buchu Leaves. With reference to some constituents, see page 119.

Cajeput Oil. The situation of this article is again normal, and does not give rise to any remarks except those of a statistical nature.

The shipments from Macassar during the year 1905 were as follows: —

to Europe	312	piculs
„ America	97	„
„ China	163	„
„ Java	1926	„
„ Singapore	1437	„
Total	3935	piculs

Camphor Oil. The peculiar situation of the camphor-market has also affected the oil. But so dark a veil lies over the whole, that at the present moment absolutely nothing can be said as to the future.

Such a large demand has arisen for the whole of the fractions which are formed as by-products in the manufacture of safrol, that we are quite unable to accumulate a stock and can only make firm offers (if at all) on receipt of special enquiries. The high prices of turpentine oil are no doubt the chief cause of the present state of affairs.

The quantity of camphor oil produced in Formosa was: —

in 1897	638603	kin[1])
„ 1898	1120979	„
„ 1899	1369887	„
„ 1900	2362108	„
„ 1901	2587186	„
„ 1902	2388135	„
„ 1903	2690370	„
„ 1904	2730388	„

The production of camphor oil in Japan is decidedly smaller.

According to the official reports from the Imperial Japanese Ministry of Finance, camphor monopoly-offices have been established in Kagoshima, Nagasaki, Kennamoto, Fukuoka, and Kobe. These

[1]) 1 kin = $1^1/_3$ lb.

offices have to deal with all matters concerning the production, collection, sale, and export of camphor and camphor oil, and also with the supervision of the camphor-monopoly.

In important places, sub-offices have also been established.

From the same source we quote the following export statistics of camphor:

	1898	1899	1900	1901	1902	1903	1904
	Yen[1])	Yen	Yen	Yen	Yen	Yen	Yen
to Australia . . .	5650	12284	47724	32904	43067	50442	26272
,, British America .	773	1421	6423	21586	20607	25592	28715
,, British India . .	38500	96583	202291	552399	507735	595736	807028
,, Straits Settlements	—	—	—	—	66549	109874	36205
,, China	1787	9864	13896	64389	93506	56282	5785
,, France	1972	257	29510	183722	33050	360275	693569
,, Germany . . .	45902	192634	64117	532771	710923	672501	146842
,, United Kingdom .	35568	29490	429412	949723	800288	491047	79026
,, Hong Kong . .	600164	939219	1017807	750603	313704	20490	87329
,, United States . .	292879	399226	1238971	810420	811007	1149925	1254255
,, other countries .	762	73517	20549	6456	4398	5680	3171
Totals	1023956	1754496	3070701	3904974	3404833	3537844	3168197

The year 1904 shows already a considerable falling off in the export[2]), and this decrease may possibly have become much larger in 1905, if any conclusion can be drawn from the constantly advancing prices.

In discussing a pamphlet by Davidson[3]) on the camphor-industry in Formosa, it is stated in the *Journal d'Agriculture tropicale*[4]) that the camphor-trees in Formosa appear to be much richer than those in Japan. In the fertile damp soil of shady valleys, the trees contain less camphor than even on bad soil in open elevated situations. Trees rich in camphor are often found alongside trees with a very low camphor-content. The distribution of the camphor in the branches, trunk, and roots is unequal, and frequently more camphor is found in one particular side of the tree than in the other. Anyone specially interested in this question finds in Davidson's pamphlet information on the content of camphor and camphor oil in the various parts of the tree at different seasons, based on studies by Professor Moriga of Tokyo. The work does not, however, say anything on the cultivation of the camphor-tree. In Ceylon, where the leaves and twigs, gathered in the same way as tea, are distilled, the cultivation of the camphor-tree is said to be carried on extensively, but up to the present no large quantities of camphor have been exported from there.

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[1]) 1 Yen = 2/-

[2]) See also Table on page 13.

[3]) L'Industrie du camphre à Formose. Imp. F. H. Schneider, Hanoy.

[4]) Journ. d'Agriculture tropicale **5** (1905), 351.

The United States Government had instructed its consuls in Japan and Formosa to supply reports on the camphor-industry of those countries, and received from its consul at Tamsui (Formosa) a comprehensive report, which represents a historical review of the camphor-industry since the introduction of the monopoly (August 1899), and which, in addition to well known facts, also mentions interesting novelties, as we find from an article in *The Chemist and Druggist.*[1])

The consul attributes the scarcity of crude camphor during the last two years to the fact, that in consequence of the Russo-Japanese war only a limited supply of labour was available in the forests; the cessation of hostilities had no doubt brought some improvement in the situation, but the consul, Mr. Fisher, does not believe that normal conditions will return until the end of 1906. The Formosa Government has engaged 2000 policemen and labourers to develop an area of 180 square miles with important camphor-forests in Northern Formosa; the Government also assists the opening up of districts in South Formosa. With regard to this, the shortage in the supply for the current year (1905) is estimated at 2400000 lbs., and for 1906 at 1000000 to 1500000 lbs.

The Japanese Government does not propose to raise the prices of crude camphor (although in case of urgent need it might be compelled to do so), in order not to stimulate still further the chemical research on the subject of the production of synthetic camphor. Whether synthetic camphor will be able to compete with the natural product when normal conditions again prevail in Japan and Formosa, is an open question. Manufacturers of celluloid will be interested to learn that it is reported that the manufacture of this article may ultimately be taken up in Japan.

With regard to the further state of affairs in Formosa, Fisher mentions that although the wages are very low, the transport of the crude material is extremely difficult. According to recent experiments, crude camphor can also be obtained from twigs and leaves, and it is the intention of the Monopoly-office to make use of this method as soon as the trees planted have reached their seventh year. Anyhow, the quantity of camphor produced in this manner will only form a small proportion of the total production.

The contract with the selling agents (Messrs. Samuel, Samuel & Co., London) runs until March 1906, and will probably be renewed. The scarcity of crude camphor exists since the end of 1903, and since that time the demand for crude camphor has been covered by immediate production, which this year was considerably lower. If no

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[1]) Chemist and Druggist **67** (1905), 975.

unforeseen circumstances occur, the prospects of a better supply of crude camphor are by no means hopeful.

The above information may be supplemented by means of a report on the same subject in the *Zeitschrift für angewandte Chemie.*[1]) According to this, the total production and export of crude camphor during the last five years was as follows: —

Year	Production in Formosa	Production in Japan	Manufacture at Kobe from camphor oil	Total production	Total export
	pounds	pounds	pounds	pounds	pounds
1900	4511184	2190175	—	6701359	6469220
1901	4725348	2669292	1635257	9029897	6717319
1902	3676060	3396908	1513795	8586763	9328399
1903	4071628	2948585	1613851	9354064	8965568
1904	4519923	900000	1979137	7399060	7372343

It is said that the Government now place three kinds of camphor on the market: „A", refined camphor; „BB", containing about 97 %; and „B", about 95 per cent. To „A" belong about 6 % of the export, and of the balance the „BB" quality slightly exceeds the „B". The American market is supplied almost exclusively with „B" quality. In order to carry out the division of the stocks in hand at the different markets without partiality, the Government endeavours to allot the shipments to the individual countries according to their participation in the exports at the time when the Monopoly was established; this comes approximately as follows: Germany 37 %, America 33 %, France 15 %, the United Kingdom 10 % and India 5 %.

Cananga Oil[2]). We have to record large sales in this oil. There are constantly direct shipments from Java on the way for us. At the present low prices this article is entitled to special attention.

Caraway Oil. The prices of caraway have on the whole suffered but slight fluctuations, so that there have been no grounds for any alteration in the prices of the oil.

It is a matter of importance for the industry which is here so highly developed, that our efforts to obtain freedom from duty for all so-called spice-seeds used for the distillation of essential oils, have at last been crowned with success. In connection therewith, the duty-free use of the residual seed for cattle-food has also been granted, and for this reason we may consider all danger past that our in-

[1]) Zeitschr. f. angew. Chem. **19** (1906), 261.

[2]) Report April/May **1905**, p. 19: read cocoa nut oil instead of "cocoa butter".

dustry will be injuriously affected by the new duty, which has been raised from 3 to 4 marks.

Our clients will profit from the resulting advantage by a difference in the price of caraway oil of about 0,60 marks per kilo, to take effect from the coming season.

We avail ourselves of this opportunity to express our thanks to the Saxon Government, which has assisted to bring victory to our suggestions, and which has also regulated the practical execution of the customs' control in a most liberal and judicious manner.

We are now in possession of official reports on the results of the caraway-harvest in Holland in the year 1905, from which we see that the estimate of our Dutch correspondents published in our last October Report, was taken much too low. We reproduce below the figures published in No. 8 of the *Nederlandsch Landbouw Weekblad* of 24th February 1906; the figures in brackets are the results of 1904 added for comparison.

Provinces	Area under cultivation in acres	Yield in bales of 50 kilos per acre	Yield in bales of 50 kilos total
Groningen	1117 (2280)	8,8 (10,7)	9864 (24688)
Friesland	65 (117)	9,3 (9,8)	606 (1147)
Drente	52 —	5,4 —	282 —
Overyssel	2 1/2 —	6,0 —	15 —
Utrecht	30 (45)	12,0 (14,0)	360 (630)
North Holland	4512 (5237)	8,5 (10,5)	38540 (54911)
South Holland	512 (660)	9,3 (9,4)	4759 (6191)
Zeeland	2070 (2505)	8,3 (11,1)	17245 (27798)
North Brabant	1900 (2557)	7,8 (9,6)	14801 (24645)
Totals	10260 1/2 (13401)	8,4 (10,5)	86472 (139790)

On the prospects of this year's harvest, we are informed under date 6th March that in Brabant less caraway is under cultivation than in 1905, but that, on the other hand, the plants are in good condition and give great promise. The same applies to Zeeland. In North Holland, much land in the Ypold district had suffered greatly from mice; for this reason the yield will be much smaller than last year.

In the Haarlem district and in Groningen and Friesland, however, the area planted is not larger than in 1905, and the plants there are looking well.

It is hoped that the mild weather will now continue until the plants are sufficiently strong to resist subsequent night frosts, as the latter might otherwise do a great deal of harm.

The old stocks, which must be taken into consideration to form a correct opinion on the situation, are said to be distincly low, but difficult to estimate.

According to the foregoing, low prices must not be reckoned upon in the coming season.

Oil of Cardamine amara. K. Feist[1]) has occupied himself with the examination of the essential oil of *Cardamine amara* L., a plant frequently confounded with *Nasturtium officinale* R. Br. The oil obtained by him by means of steam distillation of the pulverised fresh herb which had not yet blossomed, formed a brown liquid, with a pronounced water-cress odour. By the action of alcoholic ammonia a thio-urea was obtained from the oil, whose melting point (134 to 135°) and sulphur-content (mean 24,23%), correspond to those of the thio-urea obtained from secondary butyl isothiocyanate, — and, as might accordingly be expected, the body showed a feeble dextrorotation. The content of secondary butyl isothiocyanate in the fresh herb is given bei Feist as 0,0357%. Genuine water-cress, as is well known, contains phenyl ethyl-isothiocyanate.[2]) Secondary butyl isothiocyanate was first detected by A. W. Hofmann[3]) in the herb of *Cochlearia officinalis* L.

Oil of Carline Thistle. Semmler[4]) has again taken up his studies on the composition of the oil of Carline thistle (*Carlina acaulis* L.) which he commenced in 1889, and which has also formed the subject of an examination by Gadamer[5]). The oil examined by Semmler had the specific gravity $d_{19°}$ 1,0333, and the refraction n_D 1,56960. He isolated from it 12 to 15% carlinene, a monocyclic sesquiterpene $C_{15}H_{24}$ of the boiling point 139 to 141°, at 20 mm. pressure; $d_{23,8°}$ 0,8733; n_D 1,492. From the high-boiling portions of the oil, palmitic acid (melting point 62°) separated off. The principal constituent of oil of carline thistle is carlina oxide $C_{13}H_{10}O$ (boiling point 167 to 168° at 20 mm. pressure; $d_{17°}^{17°}$ 1,066; n_D 1,586; $\alpha_D \pm 0°$). Attempts made to determine the character of the oxygen atom led to no result. But on oxidation with potassium permanganate the body yielded large quantities of benzoic acid, and reduction with sodium and alcohol led to the tetrahydro compound $C_{13}H_{14}O$, which by means of oxidation with potassium permanganate gave the degradation product γ-phenyl butyric acid $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COOH$ (melting point 52°).

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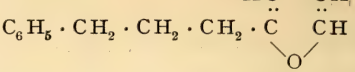
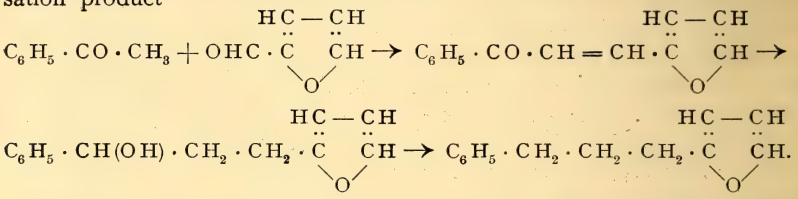
[1]) Apotheker-Ztg. **20** (1905), 832.
[2]) Arch. der Pharm. **237** (1899), 511.
[3]) Berl. Berichte **7** (1874), 513.
[4]) Berl. Berichte **39** (1906), 726.
[5]) Arch. der Pharm. **241** (1903), 44.

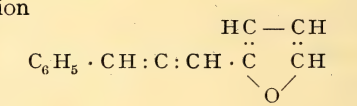
In the rest which had been oxidised away, Semmler suspected the furane ring, judging from the properties of the tetrahydro compound. The body $C_{13}H_{14}O$ would then have been a 1-phenyl-3-α-furyl-propane



A synthesis of this compound made with that end in view confirmed the supposition, and proved the identity of the two bodies. It was accomplished by condensation of acetophenone and furfurol by means of potash liquor, and subsequent reduction of the condensation product



Now, if the last-named formula belongs to tetrahydro carlina oxide, the constitution



is very probable for carlina oxide. Semmler has commenced researches for the further elucidation of this question.

Owing to the fact that the principal constituent of oil of carline thistle is a furane derivative, the supposition hitherto accepted, that the furfurol of essential oils owes its origin to the decomposition of a compound belonging to the carbohydrates, must now in Semmler's opinion be narrowed down to this, that a portion of the furfurol may also be derived from compounds of the character of carlina oxide.

Cassia Oil. The prices for 80/85 per cent. oil, which in November still fluctuated between 3/7 and 3/8, have gradually declined to 3/3 and have since remained at that level. We consider this a healthy value, and believe that a further drop is improbable. Oils of a lower content came cheaper on the usual scale. Unfortunately we had to observe repeatedly, and have also demonstrated, that middlemen had substituted oils of inferior aldehyde-content for the above highest-grade oil, which explained some remarkably cheap offers. We carry out aldehyde-determinations at all times free of charge, as it is our aim to keep the trade in this article, on which we have spent so much time and trouble, above suspicion.

Cedarwood Oil (from Hayti). A cedarwood oil sent over from Hayti, of whose botanical origin we were unable to ascertain anything more definite, but which according to the microscopical results was derived from a conifer, gave on distillation, in a yield of 4,33 %, an oil of lemon-yellow colour and the odour of the common cedarwood obtained from *Juniperus virginiana* L. But it differs from the latter by its higher specific gravity ($d_{15°}$ 0,9612), the lower rotation (α_D — 14°58′), and the higher content of alcoholic constituents (ester number after acetylation 64,0). The acid number was 2,7, the ester number 5,0. The oil was not completely soluble in 10 vol. 90 per cent. alcohol, but dissolved in every proportion in 95 per cent. alcohol.

Cinnamon Oil. The sale of this article by our firm has acquired colossal dimensions, and appears to be still capable of further expansion. This result is no doubt due to the quality of our product. The price of fine Ceylon cinnamon-chips is practically unchanged. The figures of the export in 1905 again show a considerable increase.

They were: —

to	Germany	931191 lbs.
„	the United Kingdom	358146 „
„	Belgium	284230 „
„	Italy	169344 „
„	Holland	138488 „
„	Spain	102260 „
„	America	81506 „
„	Australia	72398 „
„	Austria	63280 „
„	France	20404 „
„	Turkey	8960 „
„	Sweden	1400 „
„	India	588 „
	Total	2235395 lbs.

as against:

in	1904	2135220 lbs.
„	1903	2160352 „
„	1902	1763679 „

Citronella Oil. This important article has undergone fairly large movements during the last six months, and it would appear to us as if it had acquired now, more than before, the character of an object for speculation, for the fact that the production has not fallen off is proved by the high figures of the export-statistics which closely approach those of the year 1902, but greatly exceed those of the last two years.

The shipments in 1905 from Colombo and Galle were: —

to the United States of America	601706	lbs.
„ the United Kingdom	398700	„
„ Germany	193331	„
„ Australia	60288	„
„ France	11925	„
„ China	10499	„
„ India	3645	„
„ Belgium	2161	„
„ the Straits Settlements	216	„
Total in 1905	1282471	lbs.
as against: „ 1904	1133068	„
„ 1903	1027486	„
„ 1902	1294750	„

On the other hand, the January shipments of a total of only 19618 lbs. show such an enormous falling off, as compared with a monthly average export of about 100000 lbs., that this fact appears to explain completely the lack of available goods and the high price of the same. It is only natural that this should influence forward deliveries, and the general situation will probably not become normal again until supply and demand have adjusted themselves to some extent. As already indicated above, speculators have aggravated the situation by buying up the available stocks in Europe, a step which could be carried out with a small amount of capital in view of the comparatively small quantities of oil.

In Ceylon, the distilling already came to an end in December, and as all the labourers are employed on the rice-fields in January, the work on the citronella grass-fields came for the time being completely to an end. Stocks are already cleared out, oil for early delivery is all contracted for, so that only later deliveries come under consideration. It is therefore possible that the position may become even more acute, and that the adjustment between supply and demand will only take place when stocks have again accumulated in the principal consuming countries.

We have been able, by placing our contracts in good time, to supply our clients fully, and we have also contracts running for April shipment which are shortly due.

Under these circumstances it is for the present out of the question that prices will go back, much less that the values formerly considered normal will again be reached.

C. E. Sage[1]) reports on a Ceylon citronella oil distilled at the Experimental Station established by the Government at Peradeniya.

[1]) Chemist and Druggist **68** (1906), 355.

The examination of the dark orange-coloured oil gave the following results: $d_{15,5°}$ 0,884, α_D — 3,3°, citronellal 36%, geraniol 41%; Schimmel's test: the oil gives with 80 per cent. alcohol only a cloudy solution. This inferior solubility of a guaranteed pure oil, induces Sage to attack Schimmel's test which, as is well known, consists of this, that citronella oil must form a clear solution with 1 to 2 vol. 80 per cent. alcohol at + 20°, remaining clear or showing at most feeble opalescence when up to 10 vol. solvent are added, from which even on prolonged standing no drops of oil must separate off. Sage designates this test an arbitrary determination, which no doubt may be useful in some cases, but which cannot give information on the quality of the oil; for the latter, only the content of geraniol and citronellal are decisive. For this reason it does not appear desirable, according to Sage, to retain Schimmel's test as a criterion for the purity of the oils.

In reply to this we would point out that we also have always supported and still support the view that for the quality of citronella oil the content of total geraniol (geraniol + citronellal) is above all decisive. But such determinations frequently take up too much time for commercial practice, and for this reason an easy and quickly completed method of testing was desirable, which should at least give general data as to the quality of the oils. Such a method Schimmel's test has proved to be; experience has shown that oils can be tested by it with good results, and it has been thoroughly acknowledged and recommended by leading experts. Mr. Sage's protest will affect it all the less, as the oil examined by him also differs so widely in its specific gravity and content of geraniol + citronellal from commercial Ceylon citronella oil[1]), that a comparison with the latter appears out of place. To what cause these differences must be attributed is a matter which cannot be settled without further inquiry. What calls for particular attention is the fact that in spite of its high content of geraniol + citronellal (77%) the oil dissolves so badly. In the numerous commercial oils examined by us, we have always observed that the solubility of citronella oils increases with the content of total geraniol, and that consequently the solubility is most intimately related to the quality of the commercial oils. This fact has even induced us to introduce a "raised Schimmel's test", according to wich citronella oil mixed with 5% Russian petroleum must show approximately the same solubility in 80 per cent alcohol as the original oil[2]). We have in no single instance observed that oils of superior quality have

[1]) Common commercial citronella oil has a specific gravity between 0,900 and 0,920 (15°) and a content of total geraniol (geraniol + citronellal) about 60%; in very few cases up to 70% has been observed.

[2]) Comp. Reports April **1904**, 32; October **1904**, 20.

not stood this test, and we can with full confidence recommend it to everyone interested in the honest trade in Ceylon citronella oil, notwithstanding the opposite view taken by Mr. Sage. We hoped that in this way may be accomplished that in course of time only the best quality Ceylon citronella oil is placed on the market.

Clove Oil. During the last six months this article has, along with the prices of cloves, been subject to very considerable fluctuations, for which really no sensible reason existed. Whoever examines the situation with some care, will come to the conclusion that it depends almost exclusively upon the speculators in India, London, and Holland, who have always shown a decided preference for this article; for even admitting that the last harvest has been below normal, it is equally certain that the one of 1904 has yielded an abnormally large quantity.

According to the following Report over 1904 from the German Consul at Zanzibar, the export of cloves was: —

	Pounds.	Value: Rupees.
in 1900	11788095	2372227
„ 1901	11962069	2465373
„ 1902	10125769	2057589
„ 1903	12092138	2795980
„ 1904	14502775	4986449

It was made up as follows: —

	1900	1901	1902	1903	1904
	Quantities in pounds.				
To Europe . .	5235388	4470632	4160485	3551966	7312375
„ America . .	719600	252000	412300	852361	2056175
„ Asia . . .	5769233	7081471	5412143	7560852	4839524
„ Africa . .	63814	153966	140841	126959	94701

The shipments to America only went to New York, those to Asia to Bombay for the purpose of covering the Asiatic demand.

For the individual European markets, the exports were as follows: —

	1901	1902	1903	1904
	Quantities in pounds.			
to Rotterdam	2330764	2210420	677618	1096860
„ London	1841493	1295910	2014289	4779340
„ Hamburg	125720	425015	465995	444995
„ Marseilles	133000	188475	251664	251669

These figures show that Rotterdam has not succeeded in the last two years to carry through the attempt made to get the advantage over London.

Formerly the harvest-year was taken as the period from September to September. It is more correct to calculate it as August to August. The following figures give a review of the various harvest years since 1893: —

	from Zanzibar	from Pemba
	Quantities in frasilehs[1]).	
1893/1894	197710	402621
1894/1895	102208	307860
1895/1896	165901	413124

[1]) 1 frasileh = 35 lbs.

	from Zanzibar	from Pemba
	Quantities in frasilehs.	
1896/1897	84592	224362
1897/1898	44941	150703
1898/1899	149417	481565
1899/1900	59741	206640
1900/1901	37567	201192
1901/1902	43626	321599
1902/1903	175420	251780
1903/1904	28369	96792

From August 1904 to the end of April 1905, the following quantities were shipped: —

		from Zanzibar	from Pemba
		Quantities in frasilehs.	
1904.	August	7238	13094
	September	6143	71219
	October	4466	104308
	November	5679	80794
	December	6436	95689
1905.	January	9194	91024
	February	13655	51052
	March	9951	51433
	April	9746	30041

This shows a total quantity of 661162 frasileh for the period indicated. Up to August 1905, some 90000 frasileh will probably still be placed on the market. A crop of a total of about 750000 frasileh has not yet been recorded since the date when statistics were first kept.

The stocks of Zanzibar cloves are as follows: —

	in Holland	in London
End of 1904	3640 bales	27984 bales
„ „ 1905	6285 „	31390 „

These figures also show that Holland no longer possesses its previous importance as a clove-market, but on the contrary has been outstripped by London.

The present value of good marketable Zanzibar cloves is about 115 marks per 100 kilos, duty not paid. In view of the important part played by speculators in the determination of the value, any expression of opinion on the future of this article appears problematic.

We would still mention that the distillation of clove oil forms one of our specialities, and that for important contracts we are able to offer special advantages. The same applies to clove oil from stems.

Clove stems were shipped from Zanzibar

in	1902	1903	1904
		Quantities in pounds.	
to Europe	2158642	1738468	1001665
Asia	177252	197321	145845
America	—	678178	86755

Copaiba Balsam. For the purpose of examining and estimating the value of copaiba balsam Utz[1]) recommends the determination of the index of refraction. He employed for his examinations a refractometer of Abbe's construction, and determined the refractive index at 15°. The values ascertained for commercial balsams derived from the most diverse sources lay between 1,5088 and 1,5258. Utz is not prepared to fix definite limits of value for the individual commercial qualities, as he had no authentic pure copaiba balsams at his disposal. An adulteration of the official balsam with gurjun balsam cannot be detected by the determination of the refraction, as the two balsams have approximately the same refractive power. An admixture of fatty oils and oil of turpentine, which possess considerably lower refractive indices, can, according to Utz, be detected by determining the refraction. The determination of the polarisation of copaiba balsam, which was carried out by Utz in a solution of carbon tetrachloride 1 : 5 did not afford any definite data for a valuation.

We would caution against attaching too great a value to the determination of the refractive index by itself: when it is a question of the detection of slight adulterations, this method will fail more readily than the usual one. The same applies to Rosenthaler's test, which appears useful to Utz in many cases. Rosenthaler[2]), as is well known, uses a solution of vanillin in hydrochloric acid as reagent, and observes the colorations which occur with the balsams to be examined, both in the cold and when heated. As a violet coloration occurs both with pure copaiba balsam, and with gurjun balsam, which in the former case is feeble and disappears within a quarter of an hour, but in the latter is stronger and of longer duration, this method naturally fails where mixtures are examined.

Copal Oils. From a communication by L. Schmölling[3]) on copal oils, we abstract the following: — The most commonly used copals met with in commerce are Kauri and Manila copal, whose oils, separated from them by ordinary distillation, are employed for the manufacture of varnishes. The two kinds differ somewhat considerably in respect of content of resin acids, essential oil, etc. For further particulars we would refer to the work done by Wallach[4]) and Tschirch[5]). Schmölling now has examined the essential oils of both resins, and from this it appears that they also show considerable differences. The Kauri oil is mobile, bright yellow, has a pleasant aromatic odour,

[1]) Apotheker-Ztg. **21** (1906), 72.
[2]) Zeitschr. f. anal. Chem. **44** (1905), 292. Report October **1905**, 110.
[3]) Chem. Ztg. **29** (1905), 955.
[4]) Liebig's Annalen **271** (1892), 308.
[5]) Arch. d. Pharm. **239** (1901), 145; Report October **1901**, 56. Arch. d. Pharm. **240** (1902), 202; Report October **1902**, 31.

and does not change on exposure to the air. $d_{15°}$ 0,8677; acid number 3,0; saponification number 4,9; iodine number 288,9. With the exception of petroleum ether, it dissolves in all solvents. On distillation the bulk of the oil passes over between 150 and 160°. When tested for pinene, Kauri oil yields an abundant quantity of crystals of nitrosochloride. It does not yield a solid addition product with bromine. The oil neutralised with semi-normal potash liquor is almost completely volatilisable with steam. Its portions boiling above 170° form with bromine in alcohol-ether solution a solid addition product, which points to the presence of limonene-like bodies.

The Manila oil distils over as a pink liquid which readily becomes cherry-red on exposure to the air, and which has the following properties: $d_{15°}$ 0,9069; acid number 28,3; saponification number 45,7; iodine number 230,4. In all usual solvents, excepting petroleum ether, it dissolves completely. As distinguished from Kauri oil, only about 20% of the Manila oil distil over up to 160°, about 30% from 160° to 185°, and above 250° about 34%. With steam only about one half of the crude oil passes over. The bright yellow distillate has the specific gravity 0,8567; about 65% of it boil up to 170°. The author endeavoured without success to separate also from this oil derivatives of pinene and limonene. The distillation water of the Manila oil is rich in acids of which up to the present formic and acetic acids have been detected.

Coriander Oil. As during this season the Russian seed alone was obtainable, it was only natural that exceptionally high prices had to be asked for this oil, prices such as probably have never ruled before. In order to satisfy all demands addressed to us, we could not afford to let a single parcel of material go past us, yet we believe that our stock of oil will last until the new harvest.

Oil of Cretian Origanum. For a Sicilian oil, possibly derived from *Origanum creticum*, Umney and Bennett[1]) mention the following constants: $d_{15°}$ 0,920°; $\alpha_D \pm 0°$; phenol-content 44%, chiefly carvacrol; soluble in 2 vol. 80 per cent. alcohol, insoluble in 70 per cent. alcohol. 48% of the oil distilled over below 220°.

Oil of Cryptomeria japonica. K. Keimazu[2]) has detected in the essential oil of this conifer a dextro-sesquiterpene closely related to cadinene, which absorbs two molecules hydro-halogen, and contains two ethylene-linkings; he calls this body, whose physical constants differ from those of cadinene, cryptene. The oil contains further a polyatomic phenol, which yields a dibromine-product $C_{11}H_{14}Br_2O_3$.

[1]) Pharm. Journal **75** (1905) 860; Chemist and Druggist **67** (1905), 970.

[2]) Journ. of the Pharm. Soc. of Japan **1905**, 189. According to Pharm. Centralh. **46** (1905) 836. Comp. also Report October **1902**, 32.

Dill Oil. The cultivation of dill has increased considerably in Galicia last year, so that material for distillation is now available in abundance. The Galician seed yields an oil which is absolutely equal to that distilled from Thuringian seed.

According to the new German Tariff, dill seed has remained exempt from duty, although it really belongs to the same class as caraway, as it can also be used for alimentary purposes.

Essential oils, Sicilian and Calabrian.

From the usual reliable source, Mr. Edoardo Jacob of Messina, we received the following valuable information on the essence market.

The statistics hereafter show that last year's export, as compared with that of the previous year, has suffered a falling off amounting to 137859 kilos, value 1048830 lire, or about 14 %.

This reduction in the export is not, however, in any way due to a decline in the demand from abroad, but must be attributed to the fact that with the comparatively feeble crops of the winter-season 1904/1905, smaller quantities of oil were available for the export than in the preceding year. It has probably never happened before that the market has passed over from one season into another with stocks of all kinds of essences completely cleared out, as was the case in the autumn of 1905.

Export of essential oils in the year 1905.

	1904		1905	
	kilos	lire	kilos	lire
a) from Messina:				
to North German ports	21220	318300	20227	323632
„ Austria-Hungary	73825	1107375	78128	1250048*)
„ Belgium	3778	56670	3239	51824
„ Denmark	2666	39990	3894	62304
„ France	37302	559530	35749	571984
„ Greece	616	9240	545	8720
„ the United Kingdom	231283	3469245	212304	3396864
„ Holland	11013	165195	8818	141088
„ Russia	7956	119340	8807	140912
„ Scandinavia	5503	82545	4525	72400
„ Spain and Portugal	6722	100830	6790	108640
„ Turkey	1302	19530	1008	16128
„ the United States	389378	5840670	307692	4923072
„ South America	—	—	—	—
„ Australia	38845	582675	32039	512624
„ Egypt	1212	18180	1367	21872
„ India	1295	19425	768	12288
„ other countries incl. Italy	14436	216540	16667	266672
Total	848352	12725280	742567	11881072

*) In the exports to Austria-Hungary, the principal shipments to Germany are included, as these are sent out via Trieste.

	1904		1905	
	kilos	lire	kilos	lire
b) from Reggio:				
to North German ports	1956	29340	2095	33520
„ Austria-Hungary	28558	428370	19614	313828*)
„ France	20564	328460	21765	348240
„ the United Kingdom	25146	334295	36789	588624
„ Holland	3111	46665	1210	19360
„ the United States	23011	300150	11941	191056
„ other countries	2396	35940	1905	30480
Total	104742	1503220	95319	1525108
c) from Catania:				
to North German ports	360	3600	460	4600
„ Austria-Hungary	5940	59400	2694	26940*)
„ the United Kingdom	68	680	450	4500
„ other countries	440	4400	713	7130
Total	6808	68080	4317	43170
d) from Palermo:				
to North German ports	2410	24100	1583	15830
„ Austria-Hungary	2720	27200	3780	37800*)
„ France	2549	25490	3051	30510
„ the United Kingdom	31344	313440	11803	118030
„ the United States	4324	43240	3610	36100
„ other countries	2854	28540	2214	22140
Total	46201	462010	26041	260410

Total exports:

	1904		1905	
	kilos	lire	kilos	lire
from Messina	848352	12725280	742567	11881072
„ Reggio	104742	1503220	95319	1525108
„ Catania	6808	68080	4317	43170
„ Palermo	46201	462010	26041	260410
Total	1006103	14758590	868244	13709760

Summary of the export during the last 10 years.

Year	kilos	lire	Year	kilos	lire
1905	868244	13709760	1900	842246	10972295
1904	1006103	14758590	1899	797145	10722445
1903	864770	11964839	1898	667293	9015083
1902	1085497	15196958	1897	732092	9719133
1901	820982	12314730	1896	514067	7579424

*) Comp. Note on page 24.

Whereas for lemons and oranges a good harvest is probable, too great expectations should not be entertained for a rich bergamot-harvest, as the tree has lost much strength owing to the last abundant crop and the high oil-content of the fruit, and is in need of rest and recovery.

With regard to the individual kinds of essences, the following is mentioned: —

Bergamot Oil. In the autumn of 1905, there was a very satisfactory prospect of a good medium harvest, whilst the stocks of prompt oil had dwindled down very much; when in the course of October a brisk demand came from abroad for spot oil, the orders could only be executed at advancing prices, so that this article from 18,50 marks at the beginning of September, rose in the course of October and the first half of November to 21 marks. But the small stocks of old oil were not sufficient to satisfy the sudden demand from abroad, and as a consequence the new oils, in spite of their usual low ester-content of 30 to 31 %, were taken from the market at full prices, and at first fetched the same prices as old finest quality oil.

This, however, only lasted until more abundant supplies were placed on the market; as soon as this was the case, the article fell back to more sensible quotations.

Declining slowly, they reached about the middle of December their lowest level of 17,75 marks, to advance again in the last few days of December to 18,25 marks, owing to a more brisk demand. At this level the prices kept during the first month of the new year, and only dropped a little again in February.

If it is considered that the manufacturers have had at their disposal a good medium crop of fruit, and that moreover the fruit has given a rich yield of oil, it would not seem probable that the price of this article could be kept at the present level; but there is every indication that the opposite will be the case.

In spite of the much richer harvest, the present stocks, owing to the continued brisk export, are only very little larger than in the previous year, and there are probably at present smaller stocks of oil held abroad than in March of last year.

If it is further taken into consideration that the bergamot-tree only on the rarest occasions gives two good crops one after the other, the conclusion will be drawn that the prices of bergamot oil in the course of the next six months will hardly go lower, but that, on the contrary, it is not improbable that the summer and autumn will bring a slow upward movement in the value of this article.

Lemon Oil. The trade in lemon oil was so animated during the autumn months of last year, that the market, contrary to the view

expressed in the autumn Report, had completely disposed of its stocks of old oil before the new harvest commenced, and for this reason the new oil was able to make its appearance under the most favourable circumstances.

The old oils, in the course of October and November, fetched on the average 5 marks per kilo, and the less valuable new oil could at first not be sold at this figure, but the demand for new oil from all quarters soon became so violent that its value rose already in the middle of December to 5,10 marks, and has since advanced gradually to 5,80 marks per kilo cif. Trieste.

This movement has been promoted by various circumstances, for example, right at the commencement of the harvest by the exceptionally bad weather which prevailed in Sicily during December and January. Especially in the first half of December, continued rains greatly interfered with the work in the lemon-gardens and with the gathering of the fruit, and caused a considerable restriction in the manufacture. It is moreover obvious that the lack of old oil and the brisk demand from abroad have supplied a further lever for raising the prices; but, finally, the most particularly stubborn resistance of the manufacturers should be mentioned who, contrary to their usual habit, endeavoured to keep the market short of oil, and who thereby succeeded in obtaining the result favourable to their interests.

Since the formation of the Union of Manufacturers, to which reference has already been made on various occasions, the market must be gauged with a different measure than hitherto. Several bad harvest years following one another, and a hare-brained competition among the manufacturers, had brought this class to the verge of destitution. The natural consequence was that they were unable to hold back their products, essence and citrate of lime, but had to turn them immediately into hard cash in order to pay their workmen.

When last year the common distress had finally brought all the manufacturers together, the consequences of a regular supply corresponding to the demand immediately made themselves felt at Messina, and although the people in their excess of zeal took some false steps which finally turned out to their disadvantage, the net result of the combination was excellent for every individual member. Old debts had been paid, and everyone had a larger or smaller balance of cash in hand, so that for the new harvest the people were less dependent upon credit and upon raising money by contracts for forward delivery.

It will readily be understood that under these circumstances forward business became very difficult for the export firms, and for this reason it is all the more incomprehensible that a large Messina firm entered rashly into engagements with buyers abroad for enormous quantities of new oil at exceedingly low prices.

Such proceedings could not fail to become known or to attract observation in Messina, and the Manufacturers' Union found therein a desired opportunity to promote its own interests, by manipulating the supplies in the most skilful manner. The Union which — as already mentioned — was also greatly favoured by the weather-conditions, succeeded in keeping the market in hand, and controlling it according to its own views, so that the article under these conditions has slowly but continuously advanced from 4,75 to 5,80 marks, and has maintained itself at that level.

The conditions affecting the production, which come under consideration, now appear as follows: —

The quantity of lemons available for manufacture may be more or less equal to that of the previous year, but it appears questionable whether the quantity of oil produced from it will meet with the world's consumption. It is a fact that the approximately equal quantity derived from the crop of the winter of 1904/05 has not satisfied the demand, for the latter has used up during last year not only the entire new production of oil, but also the stocks of old oil still on hand in November 1904 both here and abroad. Although it may on the other hand be assumed that the high prices will bring about a reduction in the consumption of lemon oil, this would only dispose of the argument of prices higher than the present ones, whilst a drop in the prices before the appearance of the new harvest in November is not probable.

Two hitherto uncertain factors in these suppositions are, on the one hand the steps which the manufacturers may take in the future, and on the other, the prospects of the coming harvest. The former will constantly endeavour to push up the prices of the article, the latter may be in a greater or lesser degree favourable towards such endeavours, or they may thwart them.

With regard to the prospects of the harvest of the current year, it is at this moment impossible even to express any conjectures. The unusually large quantity of rain which has fallen during the last three months and the quiet atmospheric conditions have supplied an abundance of strength to the trees and prevented the excessive dropping of the leaves; it is therefore probable that all citrus species will blossom very abundantly. But the formation and development of the young fruit will depend entirely upon the weather prevailing in April, May and June.

Mandarin Oil. The mandarin-tree is the only one of our *citrus* species which has given a full crop in the harvest period. The fruit was very fine, well developed, and of excellent keeping qualities, that is to say exceedingly suitable for export. This has largely interfered with the manufacture of oil, and although occasionally favourable opportunities for purchase have offered themselves in this article when

superior qualities could be bought at low prices, the prices have rapidly hardened, and have gradually risen to 34 to 35 marks.

Orange Oil, bitter. The bitter orange-tree has also suffered from the frosts of the winter of last year, and has consequently produced a bad crop. The prices of this fruit also kept very high, and oil of bitter orange could only be manufactured on a limited scale.

Under these circumstances the prices of the oil set in at a very high level and rapidly advanced to 17 marks, at which figure they have since kept for faultless first-class goods.

Orange Oil, sweet. The fear expressed in our autumn Report that the new crop would prove to be a poor one, and that the new season's manufacture would only find a very limited working sphere for a remunerative yield, has been confirmed to an almost unexpected extent.

Whilst the orange-crop generally had been marked out already as a very feeble one by the injurious effect of last winter's frosts, the position of the oil manufacture especially has been extremely difficult.

In the course of the summer already the oranges at the growers' fetched prices which appeared to put the advantageous use for oil manufacture out of the question, and these prices have as a matter of fact continued in force until the very last, as with the feeble crop equal to not more than half of that of the previous year, the fresh fruit for shipment in boxes as well as for railway traffic in bulk, constantly found a ready sale at advancing quotations. As the oil manufacturer could not afford to pay such prices, there naturally followed an unusual drop in the oil manufacture, and in the present season hardly 40 % of the previous year's oil has been produced.

The prices of old oil moved during the autumn between 13,75 and 14,— marks; the new oil at once found purchasers at the same prices, and then gradually rose in October and November to 17 marks. Early in December the upward movement weakened, and a slight drop occurred; but already in the middle of that month a fresh demand sprang up, and with it a recurrence of the upward movement, which brought the article at the close of the year to 17,75 marks.

With a slow but certain advance orange oil has meanwhile arrived at 18,25 marks, and to all appearances a further considerable increase in the value is to be expected before the new harvest.

The visible stocks can at present amount to at most 5000 kilos, against 12000 kilos at the same time last year; and this small quantity has not only to meet the further demand from abroad, but also to cover the shortage existing at Messina.

Estragon Oil. Our stock is very nearly exhausted, only a very small quantity being in hand; but the herb planted out in our fields here will enable us to distil a large quantity of oil during the coming season.

Eucalyptus Oil. Our sales of the distillate of the *Globulus* species have last year acquired very large dimensions. The required quantity was supplied chiefly by Australia, Algeria only supplying a small portion. No alterations in the price can be recorded.

Since our last Report we also received a direct consignment of oil of *Eucalyptus maculata* var. *citriodora,* which had long been absent, and which has now again been included in our lists. The oil owes its beautiful balmlike odour to its principal constituent, citronellal.

According to comparative tests made by R. C. Jackson[1]) with regard to the distillation of the oils of *Eucalyptus oleosa* and *Eucalyptus Globulus,* the leaves of the second year's growth of *E. oleosa* contain the largest quantity of oil; next in order come those of the second year of *E. Globulus,* then those of the first year of *E. oleosa,* and finally those of the first year's growth of *E. Globulus.* Phellandrene could only be detected in the oil of *E. oleosa.*

According to Jackson, the Smithson Development Co. of San Rafael, Cal., works up daily 8 tons eucalyptus leaves, which are distilled with steam under pressure.

Baker and Smith[2]), who have already supplied many contributions to the chapter of Eucalypts, again give information on several West-Australian species. We only deal with this work in so far as it affects the essential oils, and would refer to the original for the botanical description of the various species.

We would make the preliminary remark, that Baker and Smith here again lay stress on the close relations which in their opinion exist between the botanical character of the eucalyptus species, and the chemical constituents of the essential oils contained in them. They specially return to this point, because the statement made by them several years ago in another place[3]) that the oil of *E. calophylla,* according to the nervature of the leaf, should contain much pinene and no phellandrene, has been confirmed by the examination now made.

1. Oil of *Eucalyptus calophylla* R. Br. (Red Gum). The oil, obtained in a yield of 0,248 %, had a dark-red colour and a turpentine-

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[1]) Amer. Soap Journ. **16** (1905), 74. Accord. to Chem. Ztg. Repert. **30** (1906), 37.

[2]) Pharm. Journal **75** (1905), 356, 382.

[3]) Journ. and Proceed. of the Royal Soc. of N. S. W. vol. **35** (1901). Report April **1902**, 41.

like odour; $d_{15°}$ 0,8756; α_D + 22,9°; saponification number 10,51; does not form a clear solution in 10 vol. 80 per cent. alcohol. The oil consists chiefly of d-pinene, and further contains cymene, sesquiterpenes, and small quantities of acetic esters. Traces of cineol only could be detected in the portions of the oil boiling about 176°; phellandrene, aromadendral and piperitone were entirely absent. The dark colour of the oil disappeared rapidly on shaking with dilute soda solution.

2. Oil of *Eucalyptus diversicolor* F. v. M. (Karri). Yield 0,825 %. The crude oil had a bright lemon-yellow colour, and a turpentine-like odour, and dissolved in 1 vol. 80 per cent. alcohol; $d_{15°}$ 0,9145; α_D + 30,1°; saponification number 53,2. A preliminary examination showed that the oil consisted chiefly of d-pinene; it also contained small quantities of cineol (less than 5 % in the fraction boiling between 172 and 181°) and about 20 % of an acetic acid ester. Phellandrene could not be detected in it.

3. Oil of *Eucalyptus salmonophloia* F. v. M. (Salmon Bark Gum). The yield of oil amounted to 1,44 %. The crude oil had a reddish colour, and had an odour of pinene and at the same time eucalyptol; it had also a faint secondary odour of aromadendral; $d_{15°}$ 0,9076 ($d_{15°}$ of the rectified oil 0,9052); α_D + 6,3°; saponification number 4,97; soluble in 3,5 vol. 70 per cent. alcohol. Constituents of this oil are chiefly pinene and eucalyptol (about 50 %) and further small quantities of aromadendral. Phellandrene was not present.

4. Oil of *Eucalyptus redunca* Schauer (White Gum or Wandoo of Western Australia). The oil obtained in a yield of 1,205 % had in the crude state a red colour; when rectified it was almost colourless. The odour of pinene predominated, besides it had the odour of eucalyptol. The remaining properties of the crude oil were: $d_{15°}$ 0,9097; α_D + 13,5°; saponification number 2,4. The oil only dissolved in 6 vol. 70 per cent. alcohol, which must be attributed to the high content of d-pinene. There were further found eucalyptol in a quantity of about 40 %, and traces of esters, whilst the higher-boiling portions (about 3 %) consisted of sesquiterpene. The test for phellandrene gave negative results. At the same time leaves of young plants ("suckers") of this eucalyptus species were distilled, and the oil thereby obtained was found identical with the one described above.

5. Oil of *Eucalyptus occidentalis* Endl. (Mallet Gum). Yield 0,954 %, colour and odour the same as of the previous oil; $d_{15°}$ 0,9135; α_D + 9°; saponification number 2,48; soluble in 1 vol. 80 per cent. alcohol. The composition is similar to that of *E. redunca*; it is only a little richer in sesquiterpene and also contains small quantities of aromadendral.

6. Oil of *Eucalyptus marginata* Sm. (Jarrah). The yield of oil differed according as the leaves used were those of old trees or of

young ones ("suckers"); in the former case 0,243 % were obtained, in the latter only 0,198 %. It should also be taken into consideration that the material was derived from different districts. In spite of this, the properties and composition of the two oils were on the whole the same, with the exception that the oil obtained from "suckers" was richer in terpenes and consequently of less specific gravity and also more difficult to dissolve.

Oil from older leaves: $d_{15°}$ 0,9117; α_D — 8,5°; saponification number 13,1; soluble in 1 vol. 80 per cent. alcohol.

Oil from leaves of "suckers": $d_{15°}$ 0,8889; α_D — 10,4°; saponification number 10,25; soluble in 5 vol. 80 per cent. alcohol.

The crude oils had a red colour, and the odour of aromadendral. The following constituents were detected: cymene, aromadendral, small quantities of pinene and eucalyptol, further geraniol (?) in the form of the acetic ester. Phellandrene was not present.

7. Oil of *Eucalyptus gomphocephala* D. C. (Touart or Tooart). The oil obtained in a yield of only 0,031 %, had a reddish colour and a rancid disagreeable odour, which reminded little of that of ordinary eucalyptus oils. It consists chiefly of terpenes, among which in abundance phellandrene, and is consequently difficult to dissolve; even with 10 vol. 80 per cent. alcohol no clear solution could be obtained. Cineol could not be detected, but an acetic acid ester was found to be present; $d_{15°}$ 0,8759; saponification number 25,74.

8. Oil of *Eucalyptus salubris* F. v. M. (Gimlet Gum). The destillation gave a yield of 1,391 % oil, which in the crude state had an orange to reddish brown colour, and a powerful aromadendral odour. $d_{15°}$ 0,902; α_D — 5,8°: saponification number 18,88. In 10 vol. 70 per cent. alcohol the oil was insoluble, but it dissolved in 1 vol. 80 per cent. alcohol. It is fairly rich in high-boiling constituents, as only 66 % passed over below 183°. In the fraction passing over above 214°, aromadendral was present in abundant quantity. There were further found in this oil: d-pinene, cymene, eucalyptol (about 10 %), and esters which probably consisted chiefly of geranyl acetate.

The comparatively high content of aromadendral of the oil of *E. salubris*, induced Baker and Smith to once more submit this aldehyde to a thorough study. It was then found, in agreement with previous results[1]), that it is really a new aldehyde, contrary to the observation which we again made recently[2]), according to which the aldehyde with a cumin-like odour which we detected in several oils, is identical with cuminic aldehyde. From this it must be concluded that two different aldehydes possessing the same odour are present in the various eucalyptus oils, of which one is cuminic aldehyde.

[1]) Report April **1901**, 33; October **1901**, 29.
[2]) Report October **1903**, 36.

For the purpose of isolating the aldehyde, which process was carried out in the usual manner with the help of the bisulphite compound, Baker and Smith used the portions of the oil boiling above 190°. The yield of aromadendral was 1,6 %. The pure aldehyde is a bright yellow mobile liquid, with a peculiar odour; $d_{22°}$ 0,95325; $\alpha_{D22°}$ — 86,2°; $[\alpha]_{D22°}$ — 90,43°; boiling point 218 to 219° with partial decomposition. Of derivatives there were produced, the oxime (melting point 86°), the hydrazone (melting point 104 to 105°, when prepared in acetic solution; the hydrazone prepared in solution of alcohol or petroleum ether melted slightly higher, but was less stable), the naphthocinchoninic acid (melting point 245 to 246°). Combustions gave figures corresponding with the formula $C_9H_{12}O$.

The compound readily absorbs bromine with formation of a liquid dibromide ($d_{22°}$ 1,4302), which on being heated splits off hydrobromic acid, when probably a monobromide remains behind. From the high specific gravity, the high refractive index, and the other behaviour, it may be concluded that the aldehyde represents a cyclic compound. The molecular refraction calculated from $d_{16°}$ 0,9576 and $n_{D16°}$ 1,5141, according to Lorenz-Lorentz, is 42,76; for $C_9H_{12}O$, the result (assuming 3 double linkings) is 42,529.

By oxidation with potassium bichromate and sulphuric acid, aromadendral was converted into an unsaturated monobasic acid (aromadendrinic acid, $C_9H_{12}O_2$). The acid dried at 105 to 110°, melted between 137 and 138°, when simultaneously a slight sublimation could be observed; the air-dry crystals, however, melted at a lower temperature, but had no constant melting point. The acid is almost insoluble in cold, slightly soluble in hot water, but dissolves readily in alcohol and ether. Combustion, and determination of molecular weight and of silver of the silver salt, gave values corresponding to the formula $C_9H_{12}O_2$. The oxidation products of aromadendral are to be examined still further later on, chiefly with the view of solving the problem of the structure of aromadendral.

The observation that the aldehydes isolated from the various eucalyptus oils showed strongly divergent rotations, led Baker and Smith to the view that aromadendral occurs in both optical modifications, which also appears to follow from the similarity of the oximes, hydrazones and naphthocinchoninic acids of the differently rotating aromadendrals. On the other hand the authors consider it also possible that in a few cases, as for example in that of oil of *E. hemiphloia*, cuminic aldehyde is present, which for the rest is undoubtedly the case in accordance with our above-mentioned examinations.

In a work which may be taken to represent a supplement to R. T. Baker and H. G. Smith's work "A research on the Eucalypts,

especially in regard to their essential oils"[1]) H. G. Smith[2]) gives the indices of refraction and a few other properties of 118 authentic eucalyptus oils, which with few exceptions had been distilled at the Technological Museum of Sydney from leaves of which the botanical origin had been determined by Baker. Smith determined the refractive indices, specific gravities, and solubilities of the oils in 70 per cent. ($d_{15,5°}$ 0,8722) alcohol at 16°, and calculates, apart from the specific refractive power, for the oils rich in eucalyptol, numbers which appear to him useful for valuing the quality of the oils, by multiplying the value of the refractive index with ten times the value of the vol. 70 per cent. alcohol required for dissolving 1 vol. oil. The oils richest in eucalyptol make the best solutions with 70 per cent. alcohol, and have the smallest index of refraction, so that they stand at the top of the series arranged by Smith; it is clear from the numbers given, that the simple determination of the solubility by itself is at least of equal value, if not more valuable, than this new and more complicated method. Smith arranges his results in tables corresponding to the compositions of the oils.

The first group consists of oils rich in eucalyptol containing pinene, and usually free from phellandrene, whose refractive index was chiefly found above 1,47 and below 1,48. To these belong:

E. amygdalina, E. Behriana, E. bicolor, E. Bosistoana, E. Bridgesiana, E. Cambagei, E. camphora, E. cinerea, E. cneorifolia, E. conica, E. cordata, E. dealbata, E. dumosa, E. eugenioides, E. Globulus, E. goniocalyx, E. gracilis, E. hemilampra, E. intertexta, E. longifolia, E. maculosa, E. Maideni, E. melliodora, E. microcorys, E. Morrisi, E. occidentalis, E. odorata, E. oleosa, E. ovalifolia v. lanceolata, E. paludosa, E. pendula, E. polyanthema, E. polybractea, E. populifolia, E. propinqua, E. pulverulenta, E. punctata, E. quadrangulata, E. redunca, E. resinifera, E. Risdoni, E. Rossii, E. rostrata var. *borealis, E. salmonophloia, E. Seeana, E. sideroxylon, E. Smithii, E. squamosa, E. stricta, E. Stuartiana, E. viminalis* var.

In the second group are found oils free from phellandrene, containing pinene, whose refractive index lies above 1,47 and below 1,48. These are the oils of *E. botryoides, E. calophylla, E. dextropinea, E. diversicolor, E. laevopinea, E. saligna, E. Wilkinsoniana.*

To the oils of the third group, free from phellandrene, containing pinene and sesquiterpene ($n_{D16°}$ above 1,48) belong the oils of *E. affinis, E. apiculata, E. Baeuerleni, E. corymbosa, E. eximia, E. intermedia, E. lactea, E. maculata, E. nova-anglica, E. paniculata, E. patentinervis, E. rubida, E. tesselaris, E. trachyphloia.*

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[1]) Sydney 1902. Comp. Report April **1903**, 40.

[2]) According to reprint kindly sent to us. Journ. and Proceed. of the Royal Soc. of N. S. Wales **39** (1905).

The fourth group is formed by the oils containing aromadendral, free from phellandrene ($n_{D16°}$ above 1,48) of *E. albens, E. hemiphloia, E. marginata, E. punctata* var. *didyma, E. rostrata, E. salubris, E. tereticornis, E. viridis, E. Woollsiana.*

Oils of the fifth group containing phellandrene and piperitone ($n_{D16°}$ above 1,48, frequently above 1,49) are those of *E. coriacea, E. delegatensis, E. dives, E. fraxinoides, E. Luehmanniana, E. obliqua, E. oreades, E. piperita, E. radiata, E. Sieberiana, E. vitrea.*

In the sixth group the oils containing phellandrene and sesquiterpene are given, whose refractive index lies above 1,48, and in some cases above 1,50. Here we find *E. acmenoides, E. angophoroides, E. capitellata, E. crebra, E. Dawsoni, E. fastigata, E. Fletcheri, E. gomphocephala, E. haemastoma, E. macrorrhyncha, E. melanophloia, E. microtheca, E. nigra, E. ovalifolia, E. Planchoniana, E. pilularis, E. robusta, E. siderophloia, E. sideroxylon v. pallens, E. stellulata, E. viminalis, E. virgata.*

The last, seventh group, includes the other not classified oils, which contain geraniol, geranyl acetate, citral, citronellal, etc. To this belong the oils of *E. citriodora, E. Macarthuri, E. Staigeriana,* and *E. aggregata.*

Of the excellent work "A critical revision of the genus Eucalyptus" by J. H. Maiden, to which we have already repeatedly referred in our Reports[1]), we have now before us the seventh part[2]), to which are appended four plates with illustrations. This part contains a detailed discussion of the following species: —

1. *Eucalyptus regnans* F. v. M. [Syn.: *E. amygdalina* Labill. var. *regnans* F. v. M., *E. amygdalina* Labill. var. *colossea* F. v. M., *E. inophloia* F. v. M., *E. fastigata* Deane et Maiden].

2. *Eucalyptus vitellina* Naudin and *E. vitrea* R. T. Baker.

3. *Eucalyptus dives* Schauer [Syn.: *E. amygdalina* Labill. var. *dives* F. v. M., *E. amygdalina* Labill. var. *latifolia* Deane et Maiden].

4. *Eucalyptus Andrewsi* Maiden [Syn.: *Sieberiana* F. v. M. var. *Oxleyensis* Deane et Maiden].

5. *Eucalyptus diversifolia* Bonpland [Syn.: *E. santalifolia* F. v. M., *E. dumosa* Benth. non A. Cunn., *E. cneorifolia* D. C. (partim) (?), *E. connata* Dum.-Cours., *E. santalifolia* F. v. M. var. *firma* Miq., *E. firma* F. v. M. herb. ex Miq., *E. cuspidata* Tausch, *E. viminalis* Labill. var. *diversifolia* Benth., *E. pachyloma* Benth.].

Oil of European Pennyroyal. There is at this moment a scarcity of this oil, as failure of the harvest has taken place both in

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[1]) Report October **1903**, 38, October **1904**, 39, April **1905**, 37, and October **1905**, 33.

[2]) Sydney **1905**.

Spain and in Algeria, and the small quantities produced have already been used up. Consumers of large quantities will therefore have to comfort themselves with hope for the coming autumn.

Since some time endeavours are also being made in Sicily to cultivate European pennyroyal *(Mentha pulegium)*. Hitherto the distilling experiments were entirely confined to plants growing wild. Such an oil has been examined by Umney and Bennett[1]). The oil, which in odour and appearance did not differ from the ordinary French or Spanish oil, was probably also derived from *Mentha pulegium*, but in its physical properties did not differ from American pennyroyal oil either. Its constants were $d_{16°}$ 0,927; α_D + 35°; content of pulegone 75 % (boiling point 212 to 220°); soluble in 2 vol. 70 per cent. alcohol.

Fennel Oil. During this season we have again distilled here large parcels of foreign fennel, and we only carry stocks of our own distillate of exceptional quality, which owing to a very high anethol-content already solidifies at + 6°. By abstracting a portion of the anethol the oil can be cheapened, and for this reason the above solidifying point should be insisted upon in placing orders. We recently examined an oil which only solidified at + 1,7°, and from which consequently the bulk of the anethol had been abstracted.

The fennel grown on fields at Lützen, only a few miles from our own establishment, unfortunately cannot compete with fennel grown abroad, the less so, as the new Tariff reasonably allows freedom of duty to foreign seed for distillation.

Reports received from Salonica state that the fennel harvest in Macedonia in 1904 has given a yield of only 200000 kilos, which in view of the harvest of 7000000 kilos of the year 1903 seems hardly credible.

With the view of increasing the knowledge of fennel oil, we submitted, when distilling a large quantity Galician fennel, the first fractions of this oil to a closer examination. The terpenes detected up to the present in the low boiling portions of common fennel oil, were pinene and dipentene[2]). Tardy[3]) claimed to have discovered also phellandrene and cymene in an oil obtained from French bitter cultivated fennel, but he failed to give the necessary proofs of this. By our renewed examination we have detected camphene as a new constituent of fennel oil, and have shown that the oil contains α-phellandrene. Cymene, however, could not be detected.

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[1]) Pharm. Journ. **75** (1905), 861; Chemist and Druggist **67** (1905), 970.
[2]) Report April **1890**, 20.
[3]) Bull. Soc. Chim. III. **17** (1897), 660.

From 1152 kilos of Galician fennel oil distilled by ourselves, two fractions of the first runnings were obtained, each 12 kilos, which possessed the following properties:

Fraction I: reddish-yellow oil with a disagreeable basic odour, which on prolonged standing acquires an intense dark-red to black colour, and which has the following constants: — $d_{15°}$ 0,8604; α_D $+42°23'$; $n_{D19°}$ 1,46793; boiling point 158 to 181° (759 mm. pressure). The bulk boils between 159 and 161°.

This fraction contains traces of basic constituents. When extracting the oil with dilute sulphuric acid and subsequently treating the aqueous acid solution with an excess of soda, there was obtained in extremely small quantity a base in the form of a faintly yellow coloured oil, which had a very unpleasant pyridine-like odour which gave rise to severe headache. It showed a feeble pyrrol-reaction and its hydrochloric solution gave with platinum chloride a platinum double salt which dissolved with difficulty in water, but the quantity of which was not sufficient for more detailed examination. This fraction of the first runnings of fennel oil further contained small quantities of aldehydes, for it imparted an intensely red colour to fuchsin sulphurous acid. But no unsoluble bisulphite compounds could be obtained by extraction with bisulphite liquor, and the oil only acquired a faint cherry-red colour after prolonged contact with the bisulphite liquor.

Fraction II of the first runnings of the fennel oil was a water white almost colourless liquid, which had neither a basic odour, nor gave an aldehyde reaction. In addition to a pronounced fenchone odour, it possessed an intensely bitter taste, and gave a strong phellandrene reaction. The constants of this fraction were: $d_{15°}$ 0,8879, α_D $+42°10'$, $n_{D18,6°}$ 1,47078, boiling point 172 to 193° (761 mm. pressure). The bulk passed over between 180 and 185°.

The two fractions of the first runnings were submitted to systematic, frequently repeated fractional distillation, in order to separate them further.

Pinene and camphene. For the detection of these terpenes served a fraction with the following properties: — colourless oil of the boiling point 155,5 to 157,5° (760 mm. pressure [distilled over sodium]); $d_{15°}$ 0,8610; α_D $+43°23'$; $n_{D24,2°}$ 1,45381. By the action of amyl nitrite and hydrochloric acid on the glacial acetic acid solution of this oil, pinene nitrosochloride of the melting point 102° was obtained, though only in a very small yield. The corresponding pinene nitrolbenzylamine base produced from it crystallised from alcohol in colourless needles of the melting point 122°.[1])

[1]) Comp. Report April **1890**, 20.

When hydrating the same fraction by means of glacial acetic acid, a yellowish oil was formed which had the odour of isobornyl acetate, and passed over at 12 mm. pressure between 62 and 108° (the bulk at 65°). On saponifying the oil portions passing over above 95° with alcoholic potash, and treating the saponification product with water vapour, a colourless crystalline mass was obtained, which possessed the odour of isoborneol, and which after being recrystallised 4 to 5 times from petroleum ether, melted at 208 to 208,5°. The melting point of the isoborneol could not be raised further.

Phellandrene. Phellandrene was detected in a fraction of the following constants: — $d_{15,5°}$ 0,8733, α_D + 34° 34′, $n_{D22,9°}$ 1,47186, boiling point 49,2 to 55° (7 mm. pressure).

The crude nitrite of the phellandrene obtained in a rather low yield, was freed from the coarsest impurities by trituration with a cold mixture of methyl alcohol and ether, and crystallised from acetic ester. Frequent repetition of the crystallisation led to the α-nitrite of α-phellandrene, which was obtained in an approximately pure state in fine colourless needles of the melting point 114° (slowly heated) or 119° (rapidly heated). The specific rotation of this nitrite in chloroform solution was ascertained as $[\alpha]_D$ — 133,4°.

From the mother liquors of the crystallisation of the α-nitrite there was obtained, by precipitating with 60 per cent. alcohol and dissolving in acetic ester, after repeating this operation several times, the β-nitrite of α-phellandrene of the melting point 103 to 104°, in small needles, grouped in the form of stars, and in a not very pure condition. But it was at any rate possible to determine that the character of the specific rotation of this nitrite (in chloroform solution) was positive (found $[\alpha]_D$ + 16,3°).

Dipentene. Dipentene[1]) was detected in fennel oil by brominating a fraction with the following properties: — $d_{15°}$ 0,8607, α_D + 37° 25′, boiling point 63 to 67° (16 mm. pressure), boiling point 177,5 to 180,5° at 748,5 mm. pressure.

The dipentene tetrabromide melted after recrystallisation from methyl alcohol and subsequently from acetic ester at 124 to 125°.

Absence of cymene. For the test for cymene, which, according to Tardy[2]) is present in French fennel oil, we employed a fraction whose constants were as follows: — boiling point 176,2 to 180,5° (762 mm. pressure), α_D + 23° 56′, $n_{D23°}$ 1,47422.

First of all this fraction was oxidised with cold 1 per cent. permanganate solution. In order to remove from this fraction any fenchone which may at the same time be present, and which cannot

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[1]) Comp. Report April **1890**, 20.
[2]) Bull. Soc. Chim. III. **17** (1897), 690.

be oxidised out in this manner, it was converted into the oxime of the melting point 161°, when the hydrocarbons were separated from the fenchone oxime by steam distillation. The yellowish oil then passing over was next further oxidised in the cold with 1 per cent. permanganate solution, during which operation its optical dextrorotation decreased gradually. Finally, there remained only 2,5 grams oil out of the 76 grams, with an angle of rotation α_D of + 12° 10′. These last oil portions were heated on a water bath with a solution of 5,04 grams potassium permanganate in 140 cc. water. But the oxidation yielded neither the p-oxyisopropyl benzoic acid characteristic of p-cymene, nor terephthalic acid. Only a very small quantity of a brown-yellow oil which could not be further identified was obtained in this reaction. Consequently p-cymene was not present in the fennel oil examined.

Oil of Fool's parsley. F. B. Power and F. Tutin[1]) have made a chemical examination of the herb of fool's parsley, *Aethusa cynapium* L., so much feared on account of its highly poisonous character. The herb gathered in July and August was extracted with alcohol in an air-dry condition, and the resulting extract distilled out with water vapour. The essential oil thereby obtained (0,015 % of the weight of the fresh herb) was at first colourless, but soon acquired a dark-brown colour, and had an unpleasant odour. In the distillation water formic acid could be detected. The distillation residue (0,8 % of the weight of the fresh herb) dissolved partly in petroleum ether. After saponifying the dissolved portion, there could be isolated from it pentatriacontane $C_{35}H_{72}$ (melting point 74°) and an alcohol (melting point 140 to 141°; $[\alpha]_D$ — 35,7°), isomeric with phytosterol $C_{26}H_{44}O$, or a lower homologue. The saponification liquor contained formic acid and butyric acid. The portion insoluble in petroleum ether, when melted with potash, yielded formic, butyric, and protocatechuic acids.

From the water which had remained behind in the retort after the distillation, there were isolated: d-mannite, melting point 165 to 166°, glucose, an amorphous dye, and a very small quantity of an alkaloid having an odour like conine. This base behaved in its chemical, physical and physiological reactions as coniine, and for this reason the toxic effect of the plant must probably be attributed to the presence of coniine in it.

Geranium Oils. During the last few years, the production has increased to such an extent in Algeria, that it has only been possible to force the demand by constant reductions in the prices. In

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[1]) Journ. Soc. Chem. Ind. **24** (1905), 938.

order to prevent a further decline in the value of this article, a moderate restriction in the production might be advisable until such time as a suitable adjustment between supply and demand has been reached.

But it would probably be difficult, if not impossible to bring the Algerian producers all under one flag.

Energetic steps have been taken in Réunion. No. 1580 of *La Patrie Créole*, of 17th December 1905, contains the official news of the formation of a Syndicate for geranium oil, the legal formalities having been gone through on the 14th December, at the Mairie of St. Pierre. The Syndicate has been formed for a period of 5 years. At the meeting of 2nd December, the producers have for the protection of their interests established this Syndicate, to which at that time ten of the most important manufacturers belonged. According to more recent information, the number of producers belonging to the Syndicate on the 29th December had already increased to 104, and were said to represent nine tenths of the whole production of geranium oil. The depot for storing the product is also established at St. Pierre. The officials have already been appointed. But a result may possibly not be expected until the enormous stocks which have accumulated at Marseilles and elsewhere in the hands of speculators, have to some extent been cleared.

The selling prices have up to the present not yet undergone any appreciable change, and there does not appear to be any intention of engineering a rise, but on the contrary of raising the value gradually, by reducing the output to 30000 kilos per annum, until a figure is reached at which the industry can continue to exist.

The question now is, whether the Syndicate will succeed in keeping control over the entire export, and whether harmony can be maintained among the participants.

The most striking comment on the steps described above forms the following table of statistics: —

In 1901	there	were	exported	13953	kilos;	the	price	was	43	francs
„ 1902	„	„	„	17193	„	„	„	„	36	„
„ 1903	„	„	„	25323	„	„	„	„	29	„
„ 1904	„	„	„	27660	„	„	„	„	27	„
„ 1905	„	„	„	38334	„	„	„	„	24	„

In our opinion the World's annual consumption is overestimated at 30000 kilos, and it has been left out of account that at the same or similar prices, the much finer Algerian distillate may generally be preferred.

The so-called Indian geranium or palmarosa oil was at the beginning of the season in October placed on the market in large

quantities, and the extremely low price led to very important transactions. Larger orders at limited prices failed through opposition of the producers, to whom the low value is no longer remunerative. For this reason a decided advance had to be paid later on, and at the present moment advantageous purchases are quite impossible. The average price of our purchases forced us to raise our quotations.

An idea of the importance of this article may be gathered from the fact that the Export of geranium oil from Bombay, from 1st July 1904 to 30th June 1905, amounted to 162990 lbs. of a value in round figures of £ 30000.

Of this quantity, quite one half consists of inferior qualities.

Exceptionally rare is this season the so-called gingergrass oil, and it remains questionable whether this oil can be offered in sufficient quantities.

A geranium oil produced in Sicily has been examined by Umney and Bennett[1]). This product, which had a quite exceptionally pleasant odour, was obtained in a yield of 0,07 % from plants grown on a dry soil. The optical rotation of the 80 % first distilling over was 11°: $d_{15°}$ 0,894; ester-content (geranyl tiglinate) 35,6 %; total geraniol 71,9 %; soluble in 2 vol. 80 per cent. alcohol; insoluble in 70 per cent. alcohol. The ester-content is therefore higher than in French or Algerian oils, but approaches very closely to the highest observed in Réunion geranium oil. In view of the small yield in which it was obtained in the distillation, it is doubtful whether the Sicilian oil will ever appear as a serious competitor against the oils met with in commerce.

Hyssop Oil. Owing to lack of distillation-material, we have temporarily been compelled to introduce the French distillate, which is inferior to the oil distilled from leaves and blossoms of the home-grown herb. But for the coming summer we have made the necessary arrangements to grow the material ourselves in sufficient quantities, so that we hope in the autumn to be able to offer again our own distillate.

Oil of Juniper berries. The high prices of the berries have now also affected the value of the common Hungarian distillate, of which only the absolutely necessary quantities can be obtained with great difficulty. This situation will continue until the coming winter,

Lavender Oil. Contrary to expectation, the distillers and principal merchants have succeeded in keeping up the high prices, and there does not appear to be a decided change in sight before the

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[1]) Pharm. Journ. **75** (1905), 860; Chemist and Druggist **67** (1905), 970.

new harvest. At the same time, the interested French parties should not aim too high, as lavender oil can be replaced by bergamot oil, whose content of linalyl acetate equals that of a fine quality lavender oil, and as consumers may strike lavender oil out of many compositions owing to its high price. It may safely be assumed that next season the demand will be considerably less, and that the public will object to pay such high prices as last year.

We also are firmly resolved to act in such manner in the future, and nothing whatever will deter us from doing all we can to bring about again a sensible state of affairs.

As regards our controversy with the firm of Lautier Fils at Grasse, concerning the ester-content of the lavender oil distilled by us at Barrême, we maintain emphatically our assertion that we have obtained in the course of manufacture large quantities of lavender oils of up to 52% natural ester-content. However, we are pleased to acknowledge that Mr. Lautier has loyally declared his willingness to give us satisfaction if we convince him of his error. This is to take place in the course of next season by expert evidence.

With regard to the ester-question, we have discussed this matter in such detail in our Report of October 1897, pages 32 to 36, and have especially done justice to the odour-test, that it would serve no useful purpose to enter once more so fully into this point in dispute. This only we would state here, that the subsequent observations, made from 1897 to the present day, have only confirmed the correctness of the position taken up by us in this question.

In a book on Pharmacy in Burgundy prior to 1803 by A. Baudot[1]), which deserves to be widely read, we find *inter alia* some details on the cultivation of lavender carried on at the Court of Burgundy in the 14th century, which we desire to quote here briefly on account of their particular interest.

In the year 1371 the then Duchess of Burgundy, who was particularly fond of lavender perfume, had a few expensive lavender stalks planted in the garden of the Castle of Rouvres and attempted at the same time the cultivation of lavender by sowing out seed. These efforts were continued with great perseverance and finally led to the desired result, so that later on it was possible to speak of a flourishing cultivation of lavender in the gardens of Rouvres. Hyssop, sage, violets, roses, and other aromatic plants were grown there with equally good results. Baudot believes that in such experimental gardens the first beginnings of our present-day botanical gardens may possibly be seen.

[1]) A. Baudot, Études historiques sur la pharmacie en Bourgogne avant 1803, Paris 1905.

Oil of Laurel leaves. Of the constituents of oil of laurel leaves, Wallach[1]) detected in 1889 pinene and cineol. Ten years later we[2]) found that eugenol is also present in this oil, whilst H. Thoms and Molle[3]) demonstrated in 1904 that the oil also contains geraniol and a small quantity of free acids (acetic, butyric, valeric acids) and also esters of acetic, valeric and caproic(?) acids. They further obtained traces of a still unknown acid of the melting point 146 to 147°. On fractional distillation of 500 gr. oil of laurel leaves of our own make, we have now succeeded in detecting two further constituents, viz., linalool and eugenol methyl ether.

The oil examined had the following constants: — $d_{15°}$ 0,930; α_D — 15° 26′. A fraction of the oil boiling at 67 to 85° (4 mm. pressure) had a distinct linalool odour. At ordinary pressure the boiling point lay between 195 to 204°.

In order to produce the linalool in the pure state, 21 gr. of the fraction were converted with sodium into the alcoholate, and the latter in ethereal solution decomposed with phthalic acid anhydride. After the impurities had been removed by dissolving the acid ester formed in soda, and extracting this solution with ether, there remained behind a solution of sodium linalylphthalate, which on being boiled with caustic potash separated off linalool. The pure linalool thus obtained and distilled *in vacuo*, had the following properties: boiling point 197 to 200° (762 mm. pressure); $d_{15°}$ 0,8715; α_D — 11° 5′; $n_{D20°}$ 1,46387. The phenyl urethane melted at 65°. On oxidation with chromic acid citral was formed.

A fraction of the oil of laurel leaves boiling at 240 to 250° was characterised by the odour of methyl eugenol. Although this compound could not be obtained in the pure state, veratric acid was obtained on oxidation of this fraction with potassium permanganate, which confirms the presence of eugenol methyl ether. The acid recrystallised from alcohol and water melted at 178°. Its silver salt gave the following values on examination: —

1. 0,2512 gr. of the substance yielded 0,0945 gr. Ag.
1. 0,1380 „ „ „ „ „ 0,0515 „ Ag.

Found	Calculated
	$C_6H_3(OCH_3)_2COOAg$.
Ag 37,62, 37,33 %	Ag 37,37 %.

Lemongrass Oil[4]). It would appear that Java will in the immediate future make competition to the Cochin distillate. Samples

[1]) Liebigs Annalen **252** (1889), 95.
[2]) Report April **1899**, 31.
[3]) Arch. der Pharm. **242** (1904), 161.
[4]) Report October **1905**, 44, read cocoa-nut oil instead of "cocoa-butter".

have already been approved many a long day since, and the first consignments may possibly make their appearance very soon. Since in the oil of *Backhousia citriodora* a new and very rich source of citral has also been discovered, which it may soon be possible to make use of in practice, the time for the exaggerated prices of lemongrass oil appears to be now past, and producers will do well to meet the trade with concessions.

A lemongrass oil originating from Ceylon examined by Sage[1]) which had been distilled at the Government Experimental Station at Peradeniya, had the following properties: — $d_{15,5°}$ 0.899, α_D — 0,2 °, citral-content 66,5 %. In alcohol the oil dissolves badly; it only forms a clear solution with 1 vol. absolute alcohol, which, however, becomes cloudy when more solvent is added.

The oil shares this deficient solubility with the West Indian and African distillates which have frequently been referred to in these Reports[2]). Both on account of the inferior solubility, and of the low citral-content, the oil must be characterised, in spite of the opposite view held by Mr. Sage, as an inferior product which cannot compete with a good East Indian commercial oil.

Linaloe Oil. The business which at one time was very much split up, has gradually passed into the hands of a few Mexican firms, who no doubt make a handsome profit out of it, for in the year 1895 we still distilled here a few thousand kilos of oil from imported wood at a cost-price which quite enabled us to compete. In the meantime the cheap sources of wood near the coast have become exhausted, and it was practically impossible to fetch the wood from a greater distance, owing to the heavy cost of transport.

The value of good oil has remained practically unchanged during the last six months.

The Cayenne distillate has a finer odour than the Mexican, and is preferred for certain products.

Mustard Oil. The prices of Indian mustard-seed have come out cheaper, so that we have again been able to undertake the regular working up of this kind of seed. Mustard oil remains an article of confidence in the fullest sense of the word. Our present selling price just covers the expenses. If a competition arises which offers pure oil from seed at still lower prices, and also supplies it pure, we shall have to give in!

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[1]) Chemist and Druggist **68** (1906), 355.

[2]) Comp. Reports October **1902**, 50; April **1903**, 23, 49; October **1903**, 46; October **1904**, 53; April **1905**, 85.

Our sale of artifical oil has increased to a considerable extent. In that line we can meet all competition.

In one of our last Reports[1]) we referred to a work on the quantitative estimation of mustard oil, by R. Firbas, in which it was *inter alia* pointed out, that if the method of estimation indicated in the German Pharmacopœia is exactly followed, the results obtained are too low, as the decomposition of the thiosinamine silver compound in the cold is not completely finished in 24 hours. By heating it, the values are raised in proportion to the period of the heating. Firbas obtained the highest results when heating in a pressure flask up to about 100°, but he leaves it an open question whether in this case the contaminations of the mustard oil, which are sparingly soluble, are not included in the estimation. We received the original work[2]) only at a late date, and now return to this subject, in order to reproduce a table in which Firbas has summarised the results obtained by him, and which will no doubt prove interesting to a larger circle of readers: —

	According to the German Pharmacopoeia IV	According to the German Pharmacopœia IV after prolonged standing	According to the Commentary to the German Pharmacopœia IV by Fischer and Hartwich	According to the Commentary after 24 hours, heating	According to the Commentary when heating to 100°	According to K. Dieterich's method (Analyt. determination of weight of the silver sulphide)
Natural oil I	84,0	84,2	95,6	96,0	96,8	98,9
do. I	83,6	83,9	94,2	—	—	—
do. II	81,4	82,1	94,7	94,9	96,1	97,4
do. III	80,2	80,2	89,7	91,6	91,8	—
do. IV	84,7	—	91,2	92,4	—	95,3
Artificial oil I . . .	76,2	—	89,4	91,4	91,6	92,6
do. II . . .	84,9	85,4	96,8	97,3	97,3	—

We have in recent times repeatedly had to make estimations of mustard oil of our own distillates, and have found Firbas' observations fully confirmed. The mustard oil determinations carried out exactly in accordance with the instructions of the German Pharmacopœia without heating, give in every case results which were about 8 % too low, and according to these no mustard oil would satisfy the requirements of the Pharmacopœia. For this reason it is at the very least necessary to follow the directions given in Fischer-Hartwich's Commentary to the Pharmacopœia, and heat the flask for a

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[1]) Report April **1904**, 63.

[2]) Zeitschr. d. allgem. österr. Apoth. Ver. **58** (1904) 222.

short time after it has been left standing for 24 hours. As already mentioned above, the period during which the flask is heated, as well as the actual temperature, are here of importance, and definite information on this point is therefore required, if comparable results are to be obtained. The method followed by ourselves agrees with the one recommended by B. Fischer and C. Hartwich in the Commentary to the Pharmacopœia: About 5 gm. of a solution of 1 gm. mustard oil in 49 gm. alcohol are mixed in a measuring flask of 100 cc. capacity with 50 cc. deci-normal solution of silver nitrate and 10 cc. ammonia liquid ($d_{15°}$ 0,960); the flask is then closed, and with frequent agitation left standing for 24 hours with the light excluded.

The flask is then placed for $^1/_2$ hour[1]) in water at 80°, during which time it is again repeatedly shaken, next cooled down to the temperature of the room, filled up with water to the mark, shaken up, and filtered. 50 cc. of the filtrate are titrated with $^1/_{10}{}^{th}$ normal solution of ammonium sulphocyanide, after adding 6 cc. nitric acid ($d_{15°}$ 1,153) and a small quantity of solution of iron alum, until a change of colour from white to red takes place. In order to ascertain the whole quantity of silver solution which has entered into reaction, the number of cc. of ammonium sulphocyanide solution used up is doubled, and the product subtracted from 50. The percentage of allyl isothiocyanate in the mustard oil is obtained by means of the following formula: —

$$\%\,CSNC_3H_5 = \frac{a \cdot 24{,}7875}{b}.$$

a = number of cc. of deci-normal solution of silver nitrate used up.
b = spirit of mustard used up in grammes.

Mustard oil determinations carried out by us in the manner described, showed in the case of natural oil a content of about 94% allyl isothiocyanate, whilst in artificial oil about 98% were determined.

Myrrh Oil. As a continuation of his work on secretions, A. Tschirch[2]) gives some information on Herabol myrrh which he, jointly with W. Bergmann, has submitted to a more detailed examination. Although the Pharmacopœias pronounce themselves very distinctly on the mother-plant of official myrrh, Tschirch considers it premature to indicate any definite species; the only thing certain is, that a *Commiphora* species of North East Africa yields the drug. From the material under examination, the so-called *myrrha electa* of commerce, the authors obtained 6 to 7% of an essential oil, by

[1]) According to Firbas the conversion is not entirely completed within that time, but we purposely do not heat for too long a period in order to avoid as much as possible the co-determination of the contaminations which are more difficult to decompose.

[2]) Arch. der Pharm. **243** (1905), 641.

exhausting the ethereal solution of the myrrh with one per cent. potash liquor, then washing with water, and after driving off the ether, distilling the residue with water vapour. The oil obtained had a honey-yellow colour, and was fairly viscid; it had a specific gravity of 1,046 and resinified readily. When exposed to the light, the oil quickly acquired a reddish-brown colour. From the residue of the steam distillation, the authors were able, after adding 1 $^0/_{00}$ potassium hydrate to obtain by further distillation another 1 $^1/_2$ $^0/_0$ of a secondary essential oil. Tschirch and Bergmann further determined the following constituents of myrrh: — α- and β-herabo-myrrholol, α- and β-herabo-myrrhol, heraboresene, a gum and an enzyme.

Myrtle Oil. In the higher boiling portions of myrtle oil, H. v. Soden and Fr. Elze[1]) have discovered a new alcohol of the formula $C_{10}H_{18}O$, which they have designated myrtenol. Myrtenol, which occurs in the oil chiefly as acetic ester, was obtained by saponification of the ester fraction with alcoholic potash liquor. By conversion into the phthalic ester acid melting at 116°, the myrtenol could be separated from admixtures of other alcohols, for example geraniol. From the phthalic ester acid, the new alcohol is obtained as a viscid, colourless oil with the odour of myrtle. Boiling point 220 to 221° (751 mm. pressure); 79,5 to 80° (3,5 mm. pressure); $d_{15°}$ 0,985; α_D + 49° 25′. Myrtenol can be acetylised quantitatively, and appears to be a primary cyclic terpene alcohol.

Nepeta Oil. A Sicilian nepeta oil, whose more exact origin could not be determined, has been examined by Umney and Bennett[2]). Its constants were $d_{16°}$ 0,927, α_D + 12°; total alcohol content (menthol) 22,2 $^0/_0$; ester content (menthyl acetate) 3,3 $^0/_0$; soluble in 2 vol. 70 per cent. alcohol. Small quantities of a ketone, possibly menthone or pulegone, appeared to be contained in the oil.

Neroli Oil. The most recent information on the prospects of the harvest of orange-blossoms in the South of France, which commences next month, are very unfavourable. The frost of the last days of March is said to have destroyed half the blossoms. The high prices may consequently continue in force. It is an undeniable fact that these high prices have greatly interfered with the sale of the natural oil, and have in many cases led to the introduction of the artificial oil which is now produced in such a high degree of perfection. Although under normal conditions of value the two oils may go alongside each other, when the difference is so enormous as last year, it becomes a matter of necessity for many to make use of the advantages which the artificial product offers.

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[1]) Chem. Ztg. **29** (1905), 1031.
[2]) Pharm. Journal **75** (1905), 861; Chemist and Druggist **67** (1905), 970.

The matters in dispute between the manufacturers and the growers in the South of France are still unsettled. The latter, to the number of about 1400, have jointly established works at Vallauris, said to be capable of distilling 1 400000 to 1 500000 kilos blossoms. Operations will be commenced there if the manufacturers refuse to pay a price for the blossoms which enables the growers to earn a living, and to continue the cultivation.

Orris Oil. On the present position of the orris-root market we receive from our friends in Florence the following information: —

According to our previous report the quantity at disposal at the beginning of September 1905 amounted to . . . . . about 560 tons
added to this, the result of the last harvest . . . . . „ 650 „
makes a total of about 1210 tons.

If we deduct the shipments from the beginning of September 1905 to the end of February 1906 . . . . . „ 550 „
there remains at disposal, at the end of February 1906 . . about 660 tons.

The export during the present season will apparently be a very large one, as from the beginning of September 1905 to the end of February 1906, that is to say in only 6 months' time, already 550 tons have been shipped, as against a total export of only 500 tons during the preceding 12 months, 1st September 1904 to 31st August 1905.

As compared with the last crop (1905) of 650 tons, we had in 1904 a crop of 670 tons, in 1903 of 750 tons, and in 1902 of 1000 tons.

The quality of the last crop has with few exceptions again turned out inferior, as too little care is bestowed upon the cultivation. The new plantings have again been reduced by about 10 %. The demand has, since the beginning of September, constantly been good; France especially has bought a good deal, and is still in the market. The consequence is a continued advance in the prices. At the commencement of the harvest it was possible to buy assorted roots at 36/37 marks cif. Hamburg; now they are quoted 48/50 marks. Of seconds, which were last paid 45 marks cif. Hamburg, hardly anything can at present be obtained. With regard to the prospects of the next harvest we believe that, in view of the smaller quantities planted out in recent years, not more than 500 tons may be reckoned upon. The further movement of the prices during the present season will naturally depend in the first place upon the demand; if this should continue as at present, not much would remain of the existing stocks by the time of the new harvest, and this might easily have an upward effect upon the prices of the latter. The big demand from France appears to point to the fact that the old stocks there have been used up, which is all the more probable, as France was buying so little in the previous year. This would also explain the small export of but 500 tons during the 12 months from 1st September 1904 to 31st August 1905, whilst the world's annual consumption is estimated at about 900 tons.

Veronese orris has also advanced considerably. The so-called "*mercantile*" quality, which last autumn could be bought at 22 marks, now fetches 33 marks cif. Hamburg, with very small stocks. In the other Veronese qualities, No. 1 and No. 2, a great scarcity also exists, as the last crop, as is well known, was a very small one.

Taking all together, the probability is that high prices of orris-root must be looked for in future.

After such an important advance in the prices, amounting now to about 50 %, it was impossible to retain the quotations of orris oil which had been based upon the lowest purchase prices of the previous year. We have, however, raised our quotations for the present so little, that the advance represents a scarcely noticeable charge to the consumer, and in view of the situation we can only advise our friends to lay in an abundant supply at the present prices.

Patchouli Oil. After the prices had been forced down to the extreme limit, the downward movement has come to a stop. Good, healthy patchouli-leaves from Penang reached their lowest level in December last year with 25/- per cwt., but they advanced shortly afterwards to 28/- and cannot now be bought below 30/-. The low prices of oil have been largely taken advantage of; they bring profit to the perfumer in a double sense, as it is a well-known fact that the quality improves by prolonged keeping.

In the Botanical Garden of Buitenzorg there are three varieties of patchouli: I. *Patchouli fleurissant* (*Pogostemon Heyneanus* Bth. ?), II. *P. de Singapour* (*Pog. tomentosus* Hassk.?), III. *P. de Java* (a variety of *Pog. tomentosus* Hassk.?), whose essential oils, according to A. W. K. de Jong[1]) possess the following properties:

	I.	II.	III.
$d_{25°}$	0,922	0,949	0,929
$[\alpha]_{D\,25°}$	— 16° 10′	— 51° 24′	42° 48′ [2])
Soluble in:	10 vol. 90 per cent. alcohol	6 vol. 90 per cent. alcohol	0,75 vol. 90 per cent. alcohol
Distillation at 740 mm. up to 250°:	130 to 250° = 17 %	230 to 250° = 2 %	145 to 250° = 10 %
250 to 270°	50 %	60 %	70 %
270 to 280°	16 %	20 %	8 %
280 to 300°	10 %	10 %	6 %

The oils II and III contained Gladstone's azulene. The action of concentrated sulphuric acid left unchanged 17 % of I, 22 % of II, and 20 % of III, from which was obtained by distillation a sesquiterpene (boiling point 260 to 263° at 740 mm. pressure) for which the author proposes the name dilemene. $[\alpha]_{D\,25°}$: II. — 1°, III. — 1,5°; $d_{25°}$: II. 0,915, III. 0,897. This sesquiterpene de Jong considers possibly identical with the sesquiterpene (boiling point 273 to 274° at 760 mm pressure: $[\alpha]_D$ + 0° 45′; d 0,930), discovered by von Soden and Rojahn[3]) in patchouli oil.

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[1]) Recueil des trav. chim. des P.-B. **24** (2905), 309 to 312, Buitenzorg. Acc. to Chem. Centralbl. **1905**, II. 1180.

[2]) The sign denoting the direction of the rotation is not mentioned in the Report.

[3]) Berl. Berichte **37** (1904), 3354. Report April **1905**, 61.

According to a communication by P. Serre[1]) on the patchouli industry in Java and the Straits, the patchouli plants cultivated there also originate from *Pogostemon patchouli;* when fully developed they reach a height of 2 to 3 feet. The harvest of the leaves (which are sent to Europe in a well-dried state) commences as soon as the plants are 6″ high; every six months the leaves are stripped again. The Malays put patchouli leaves in their mattresses and clothes to keep away insects. The yield of oil produced in the factories of those countries amounts to only a few per cent., owing to defective distilling apparatus; the yellow-green to dark-brown oil is very thick, and separates off crystals of patchouli alcohol. With the plants imported in Java, good results have been obtained up to an elevation of 1600 feet, but in Serre's opinion the oil obtained is of a lower quality than that produced in the Malacca Peninsula.

Peppermint Oil, American. The reports received from the principal districts of the peppermint oil production all agree, that the damage done to the fields by the winter-frosts turns out to be severe. The total absence of snow has allowed the frost to act direct on the plants, and to destroy a number of them, especially in Michigan. For this reason a certain falling off in the production must be expected next autumn, but against a too pessimistic interpretation of such communications should be warned, for experience shows that interested parties are apt to exaggerate, and in the course of the summer the traces of such damage very often dwindle down. But what should be specially taken into consideration, is that the quantity planted out has been considerably increased during the last two years, since the good prices obtained had again made the cultivation and distillation of peppermint a very remunerative occupation.

The present opportunity has naturally been taken advantage of in America to drive up the market-prices of crude oil, and the European markets have also followed the lead from the other side. The increase in the price from the beginning of January to the present moment amounts to fully 20%. Normal crude oil cannot be purchased to-day below 3,25 dollars.

Our New York branch, whose purchases come to about 30000 lbs. per annum, called our attention to the superior quality of the 1905 oil already on shipping the first parcels of the distillate of that year, and we have found this fully confirmed. In Japan it is hoped that America, in consequence of the present state of affairs, will appear as a heavy buyer of Japanese oil. There is nothing in this, if the latter is not used for mixing with the American oil, such as was the case some 3 or 4 years ago, at the time of the $ 5,— price. In

[1]) Journ. d'agriculture tropicale **5** (1905), 369.

any case, it will be advisable to pay in future close attention to the common marketable qualities.

When fixing the prices of our two brands, we took into account the advantageous purchases made by us before the "frost"-situation, and we consider ourselves justified in advising a moderate cover at the present quotations. We will in future, as heretofore, do all we can to further the interests of the consumers of our brands, and will as energetically oppose any unwarranted or exaggerated upward movement, as we have successfully done in former years.

On the 28th December 1905, the U. S. Department of Agriculture published a work by Alice Henkel, Assistant examiner of drug-plants, which gives interesting and partly new information on the history, cultivation, and utilisation of the peppermint-plant, and of which we reproduce below an abstract, from which the purely botanical details have been omitted: —

One of the most important oils produced in the United States is the one obtained from the peppermint-plant and varieties. The three kinds of mint which are cultivated in that country, are the so-called American mint (*Mentha piperita* L.), the black mint (*Mentha piperita vulgaris* Sale), and the white mint (*Mentha piperita officinalis* Sale); the two last-named are varieties of the first.

The peppermint or American mint is now grown in many parts of the Eastern States, and is found in the damp soil of New England States as far as Minnesota, and to the South as far as Florida and Tennessee. The black mint is harder and yields more than the other two kinds, and comes under consideration for practically all peppermint-farms. The white mint no doubt yields a very fine oil, but is little cultivated, owing to its sensitiveness and small yield.

Peppermint was first grown on a larger scale in 1816 in Wayne County, N. Y. Neighbouring counties also took up the cultivation, but Wayne County was and remains to this day the principal peppermint district in the State of New York.

The cultivation was then gradually extended to the Ashtabula, Geauga, and Cuyahoga County in Ohio, and also to Northern Indiana. Roots were introduced from Ohio into St. Joseph County, Michigan, and the first roots were planted in the Pigeon prairie in the year 1835. In the following years, the cultivation in the last-named State extended more and more, and since 35 years it has developed into the greatest peppermint producing section of the United States.

About 1844, an interesting "peppermint oil monopoly" was taken up by a New York firm, which apparently brought the cultivation in the State of Ohio to an end.

The first step consisted of this, that the firm sent a representative to Liverpool, to make inquiries about the comsumption in England, which at that time is said to have amounted to 12000 lbs. per year. Another agent was sent to the West to ascertain the annual production, with the result that Wayne County N. Y. did not produce enough, Ohio too much, and the plantations in Michigan about the above-mentioned quantity of the English consumption. The agent of the firm now bound the producers of the States of New York and Ohio, under a high penalty, to plough up their peppermint fields, destroy the roots, and neither plant mint nor sell roots or oil for a period of five years. In consideration of this the producers received an allowance of 1,50 dollar per acre. The firm secured by contract the entire oil production of St. Joseph County, Mich., at the price of 2,50 dollars per lb. for a period of five years. The extension of the plantations and the sale of roots were also forbidden by contract. The producers carried out their engagements for three years, after which time the New York firm no longer laid stress upon the observance of the contracts, as it had meanwhile made a fortune out of the monopoly.

Since that period the area devoted to the cultivation of peppermint in Michigan has constantly extended, and Northern Indiana with the principal producing centres St. Joseph, Steuben, and La Grange County, also places continuously important quantities of oil on the market. In Ohio the cultivation has been given up, and in the State of New York the production has for years been cut down, until recently it has again acquired larger dimensions. Whilst in the year 1889 in Wayne County 3325 acres were planted with mint, the cultivation gradually declined until in 1899 it amounted to 300 acres, but it rose again to 933 acres in 1905.

The foregoing Report mentions finally that the good prices of oil of the last few years have induced many planters in the most diverse places to extend the cultivation of peppermint. This is not only the case in Michigan and Indiana, but also in the State of New York. For this reason a larger production of oil may be anticipated for the next few years, if favourable conditions prevail, and this is bound to have a depressing effect on the quotations.

The state of the market must therefore be kept under close observation, for the expenses of the cultivation amount to 12 to 14 dollars per acre, and those of the oil-distillation to 25 cents per lb. oil, so that the market-price of the oil may readily again fall below the cost of production.

Peppermint Oil, Japanese. The confidently expected drop in the prices has up to now been prevented by speculative enterprise. Japanese exporters are said to have sold large parcels of oil and

crystals for forward delivery at low prices, and to be compelled shortly to cover these. Knowing this, the Japanese are holding back offers, although the stocks in Japan must still be very heavy, and at the end of year were estimated at 150000 to 180000 lbs. The stocks in London and Hamburg are probably also fairly large, and moreover were bought dear, so that in both these places the tendency will be to keep the prices up.

The disposition in Japan is at this moment firm. The Japanese explain this in the following manner: — the cultivation of peppermint in the coming season will probably be greatly restricted, as the farmers do not find the present prices remunerative. The intention is, in case of need to warehouse the stocks and wait for better times. In this connection, however, the Japanese appear to forget that peppermint oil is not an article which lends itself to warehousing, as the quality suffers from age and from prolonged contact with the tin of the cases. To store the oil up for many years is therefore out of the question.

In our opinion the present value is low, and it does not appear advisable to speculate for still lower prices.

The total shipments from Japan of liquid oil and menthol during the year 1905, are as follows: —

	Peppermint Oil	Menthol
January	32325 kin.	23391 kin.
February	29400 „	21304 „
March	25345 „	25982 „
April	19350 „	15635 „
May	7521 „	14517 „
June	942 „	6472 „
July	5321 „	5193 „
August	8409 „	6167 „
September	7032 „	1725 „
October	6567 „	8137 „
November	13470 „	15377 „
December about	12000 „ about	13000 „
Total	167684 kin	156900 kin
		167684 „
Total oil and crystals		324584 kin à 600 gm.
		= 194750 kilos.

According to the Financial and Economic Year book of Japan, published by the Imperial Ministry of Finance at Tokyo, the total value of the shipments of peppermint oil to the individual countries during the previous five years was as follows: —

	1900	1901	1902	1903	1904
	Yen	Yen	Yen	Yen	Yen
to British America .	—	—	—	2606	27450
„ France	—	3436	7459	12593	60326
„ Germany . . .	16911	16942	50889	92351	95399
„ the United Kingdom	—	13942	32175	57854	122738
„ Hong Kong . .	28335	69572	59800	86691	163676
„ the United States .	—	—	12309	20682	74105
„ other countries . .	5725	4546	2215	4839	15255
Total	50971	108238	164847	277616	558949

The Report of Roure-Bertrand fils[1]) of Grasse contains an interesting work by Marin Molliard on "*Menthe basiliquée*". Under this designation is understood a degeneration of the peppermint plant frequently observed in the South of France, which shows itself in a completely altered appearance as compared with the normal plant[2]). The change consists of this, that the stalks and twigs which normally would run into inflorescences, never again form blossoms, but only leaves closely bunched together. The large leaves at the base of the altered twigs also show in their shape characteristic differences from the normal leaves of the peppermint; they are, namely, contrary to the latter, almost sessile, have a hand-shaped nervature, and a scarcely dentated edge. The stalk of the altered plant, of which the section is originally square, shows in the ramification a more and more circular section. These morphological and anatomical changes are caused, according to Molliard's researches, by a parasitism of acarides belonging to the group phytoptides and the family eriophyes. We would in this place only refer to the detailed description of the parasite to which Molliard has given the name "Eriophyes menthae". The acarides already attack the twigs of the peppermint plant at the moment when they are just breaking through the earth. The outer leaves undergo the least change, as they are soon left by the parasites, which endeavour to settle at the point of the newly forming leaf-buds. The younger leaves, however, which have to develop entirely in the presence of the parasites, suffer most from the destructive action of the acarides.

Up to the middle of July the parasites are found in large numbers on the twigs altered by them; they then disappear gradually. They hibernate apparently in the earth close to the stem or on its surface,

[1]) Reports of Roure-Bertrand fils, Grasse. October **1905**, 3.
[2]) Comp. also Gildemeister and Hoffmann, "The Volatile Oils", p. 649.

in order to produce again the same malformation in the following year. Up to the present no practical remedy is known to protect the peppermint plant from the attack of the eriophyes.

In continuation of a previous communication[1]) on Sicilian peppermint oils, Umney and Bennett[2]) report on a third oil of the same origin, which had been distilled in July 1905. It agrees completely in its properties with the oil distilled in July 1904: — $d_{15°}$ 0,906; α_D — 21°; total menthol 41,6%; ester (menthyl acetate) 6,0%; free menthol 36,9%; soluble in 3 volumes 70 per cent. alcohol.

Petitgrain Oils. Whilst the real petitgrain oil, the essential oil from the leaves and twig-ends of the bitter orange (*Citrus bigaradia* Risso) has already repeatedly been examined, the constituents of the essential oil obtained from the leaves and twigs of the sweet orange (*Citrus aurantium* Risso) are still unknown. An examination made by G. Litterer[3]) according to the usual methods, disclosed as principal constituents citral, geraniol, camphene and limonene. The constants of the oil were; $d_{15°}$ 0,8603, α_D + 56° 46′, $n_{D20°}$ 1,472.

The citral, representing 4% of the oil, was isolated by shaking with sodium sulphite liquor. The semicarbazone melted at 163°, the citryl naphthocinchoninic acid at 197°. The portion of the oil from which the citral had been removed contained 4,1% ester, calculated for $C_{10}H_{17}O \cdot COCH_3$. The acetylation showed a content of 19,7% alcohols of the formula $C_{10}H_{18}O$. Of these, 12,7% combined with phthalic acid (geraniol). After saponification of the portions separated from the citral, they were fractionated, and in the terpene fractions were detected, camphene by conversion into isoborneol, and limonene by its tetrabromide (melting point 104°). In the higher-boiling fractions linalool was apparently also present, besides geraniol, but its presence could not be proved owing to the small quantity. Geraniol was isolated by means of the calcium chloride compound.

An oil[4]) produced by the same author[5]) from the leaves and twig-ends of the lemon tree (*Citrus limonum* Risso) had the specific gravity 0,8824 at 15°; α_D + 21° 08′; $n_{D23°}$ 1,4725. From this oil 24% citral were isolated. The semicarbazone melted at 162 to 164°, the citryl naphthochinchoninic acid at 197°.

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[1]) Report October **1905**, 57.
[2]) Pharmac. Journal **75** (1905), 860; Chemist and Druggist **67** (1905), 970.
[3]) Bull. Soc. Chim. III. **33** (1905), 1079.
[4]) An oil of this kind has repeatedly been described by us. Citral had also been detected by us already before. Comp. Report October **1896**, 59; April **1902**, 79; April **1905**, 64.
[5]) Bull. Soc. Chim. III. **33** (1905), 1081.

Citronellal could not be detected. The oil from which the citral had been removed contained 10,5 % ester, calculated for $C_{10}H_{17}H \cdot COCH_3$, and 11,2 % free geraniol. After saponification, limonene was detected (by the tetrabromide) in the terpene fractions. Camphene could not be obtained with absolute certainty. In the higher-boiling fractions linalool is probably present. The presence of geraniol was proved by the boiling point, and the formation of citral.

In a Sicilian oil of lemon leaves (*Petitgrain citronnier*) Umney and Bennett[1]) ascertained the following physical constants: $d_{15°}$ 0,873, α_D + 26°; ester content 9,4 %; aldehyde content 29 %; total content of alcohol 38,9 %. The first 30 % of the product passed over between 175 and 180°.

Pimento Oil. We offer only our own distillate, and have again been able to reduce its price.

Pine-needle Oils. There is a great scarcity of all kinds, as far as pure original distillates are concerned. Particularly scarce is the oil of *Pinus pumilio,* the so-called "Latschenkiefer", and an examination of the products met with in commerce under this name has led to the result that they are almost without exception substitutes. Further, this oil from the "Latschenkiefer" grown in the lowlands appears to be of a different character to that from the trees in the Tyrolese mountains. We hope that we shall succeed in clearing up this matter by comparing our own distillates, and this seems to us all the more necessary, as the oil of *Pinus pumilio* finds a constantly growing use as a medicament.

The production of the very popular oil from the Siberian pine-needle, *Abies Sibirica,* appears to have been neglected entirely owing to the internal troubles in Russia; at present it can only be obtained in small parcels, which is very annoying, as the oil has become thoroughly introduced.

The oil from the needles of *Abies alba* is also supplied in insufficient quantities, but as it is not officinal, it can in case of need better be dispensed with than the oil of *Pinus pumilio.*

It is much to be hoped that new sources of supply of good conifer-distillates will soon be opened up.

We have recently had occasion to distil ourselves oils of *Pinus pumilio* and of the needles of *Abies alba,* and we give below the properties of the distillates obtained by us. The distillation material had been obtained from Styria, and was worked up cut in very small pieces.

Oil from *Pinus pumilio.* The yield of crude oil (coloured yellow) was 0,41 %. The oil begins to boil at 170° (746 mm.); at 203°,

[1]) Pharm. Journal **75** (1905), 861; Chemist and Druggist **67** (1905), 970.

67 % had distilled over; $d_{15°}$ 0,8685; α_D — 11° 3′; acid number 1,4; ester number 16,8 = 5,9 % bornyl acetate; soluble in about 5,5 or more vol. 90 per cent. alcohol.

Oil from the needles of *Abies alba.* Yield 0,56 %; $d_{15°}$ 0,8852; α_D — 34° 55′; acid number 0,9; ester number 17,5 = 6,1 % bornyl acetate; soluble in about 6,5 and more vol. 90 per cent. alcohol. The oil begins to boil at 162°; up to 185°, 55 % passed over.

An oil from the needles of *Abies alba,* distilled from the same material but cut up in coarse pieces, showed slight differences which are probably due to a somewhat smaller content of sesquiterpene as compared with the oil just described: — $d_{15°}$ 0,8845; α_D — 35° 34′; acid number 1,3; ester number 21,2 = 7,4 % bornyl acetate; soluble in about 5,5 and more vol. 90 per cent. alcohol.

These oils from the needles of *Abies alba,* distilled by ourselves, have a higher specific gravity than the distillates originating from Switzerland and the Tyrol, in which it lies between 0,869 and 0,875. But in the distillates produced in Upper and Lower Austria we have always found higher specific gravities, up to 0,886, so that the origin should be taken into account when judging the oils.

Oil from *Pinus laricio.* Two distillates sent to us, said to be derived from the needles of *Pinus laricio* Poiret, behaved as follows:

a. $d_{15°}$ 0,8646; α_D + 8° 17′; ester number 2,9 = 1,0 % bornyl acetate; soluble in 8 to 9 and more vol. 90 per cent. alcohol.

b. $d_{15°}$ 0,8701; α_D + 3° 29′; ester number 9,8 = 3,4 % bornyl acetate; soluble in 8 vol. 90 per cent. alcohol.

Both oils were colourless, and had a pleasant balsamic odour.

Oil from *Pinus maritima.* E. Belloni[1]) reports on his examinations of the essential oil from the shoots of *Pinus maritima* Mill. On distilling the fresh shoots gathered in the South of France, the author obtained a yield of 0,681 % and when using dried shoots of 0,517 %, of a bright-green essential oil possessing an aromatic taste and characteristic pine needle odour. Belloni determined the following constants: —

A. Oil from fresh shoots: $d_{15°}$ 0,8810, α_D — 23° 46′, $[\alpha]_{D\,15°}$ — 26,518°, acid number 0, ester number 7,9; saponification number 7,9, ester 2,77 % (calculated for $C_{10}H_{17}O \cdot CO \cdot CH_3$), combined alcohol 2,13 %.

B. Oil from dried shoots: $d_{15°}$ 0,8963, α_D — 20° 15′, $[\alpha]_{D\,15°}$ — 22,355°, acid number 5,43, ester number 8,27, saponification number 13,7, ester 2,92 % (calculated for $C_{10}H_{17}O \cdot CO \cdot CH_3$); free alcohol 11,9 %; combined alcohol 2,28 %, total alcohol 14,18 %.

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[1]) According to reprint kindly sent us. "Sull' essenza di gemme di *Pinus maritima* Mill." Milan 1905. Estr. dall' Annuario della Soc. Chim. di Milano **11** (1905). Comp. Chem. Centralbl. **1906**, I. 360.

The oils are insoluble in 80 per cent. alcohol, soluble in 10 vol. 90 per cent. alcohol; they are miscible with 95 per cent. and stronger alcohol.

On fractional distillation in a Ladenburg flask, there passed over, of oil A: between 155 and 170°, 58% (α_D — 27° 50′), between 170 and 190°, 20% (α_D — 31° 40′), residue 20%. Of oil B there distilled between 155 and 170°, 42% (α_D — 26° 42′), from 170 to 190°, 20% (α_D — 29° 34′), residue 37%.

The oil of *Pinus maritima* contains no aldehydes; the free acid of the oil obtained from dried shoots consists chiefly of caprylic acid (about 1,396%). In the formation of ester, only lower fatty acids appear to take part, probably acetic acid, propionic acid, caprylic acid, and laurinic acid. The bulk of the oil, according to Belloni, consists of l-pinene, of which he determined the following constants: $d_{15°}$ 0,86186, $[\alpha]_{D\,15°}$ — 29° 30′, boiling point 155 to 157°. (Nitrosochloride melting point 103°, nitrolpiperidide melting point 118°.) Phellandrene and sylvestrene could not be detected in the fraction passing over from 170 to 190°, but the presence of limonene is probable, either in the optically active form, or inactive as dipentene. The alcohols of the oil could not be identified; although the odour pointed to the presence of borneol esters, it was not possible to isolate borneol.

When producing the pinene nitrolpiperidide, Belloni observed that, when the alcoholic solution of the nitrosochloride is heated for a prolonged time with piperidine on the water bath, there are formed, in the place of pinene nitrolpiperidide, needle-shaped crystals of the nitrosopinene (melting point 131 to 132°). Piperidine acts therefore, with prolonged heating, the same as potassium hydrate or diethylamine, which convert nitrosochloride into nitrosopinene.

Rose Oil. The prices of the better-class brands of really pure quality have kept at the same level throughout the season, but ordinary market-qualities, of which the bulk of the sales consists, could be bought about 30% cheaper. The official export-figures of the last two years are as follows: —

Rose oil export from 1st January to 31st December.

	1905	1904
to Austria-Hungary	23 kilos	23 kilos
„ the United Kingdom	891 „	472 „
„ Germany	714 „	853 „
„ Turkey	230 „	578 „
„ France	1529 „	1445 „
„ the United States, Russia, Italy, Belgium, etc.	1929 „	1023 „
	Total 5316 kilos	4394 kilos

The stocks in hand of the various qualities are estimated at about 650 kilos.

With the exceptionally mild winter, the rose-fields have up to the present suffered no damage whatever, and at this moment the prospects of the new harvest are very favourable. It is to be hoped that they will not be affected by belated night-frosts. With regard to the yield, nothing certain can be said before the end of May.

During the examination of consignments of rose oil, W. H. Simmons[1]) observed in two cases the presence of ethyl alcohol. As in both cases only very small quantities of alcohol (0,65 and 1 % respectively) were detected, Simmons attributes their presence more to an accident than to an intentional adulteration, but in the case of an expensive article like rose oil a small alcohol-content is also important, especially when it is a question of the purchase of large quantities. Simmons does not believe that processes of fermentation play here a part, such as we have once before observed with our own distillates[2]), as the samples belonging to the consignments did not contain alcohol.

Simmons avails himself of the opportunity to point out that the index of refraction may occasionally be of some value for judging rose oil; he mentions 1,4600 as the lowest permissible value for 20°. We have observed in good oils at 25° refractive indices between 1,452 and 1,464[3]).

Rosemary Oil. Both the Dalmatian and the French oils suffered from a slow demand. The distillers of the former may possibly be compelled to make concessions in the price, in order to dispose of their product. The manufacturers in the South of France already show themselves more accommodating.

Sandalwood Oil. The parcels of sandalwood purchased by us at the last auctions, have now all arrived.

The official statement of the 15th August 1905 showed the following quantities for sale: —

District	Koti	Date of auction	Approximate quantity
Shimoga	Tirthahalli	14 November 1905	200 tons
do.	Sagar	18 „ „	200 „
do.	Shimoga	22 „ „	370 „
Kadur	Tarikere	25 „ „	150 „
do.	Chikmagalur	28 „ „	350 „
Hassan	Hassan	2 December „	200 „
Bangalore	Bangalore	6 „ „	130 „
Mysore	Seringapatam	9 „ „	250 „
do.	Hunsur	12 „ „	450 „
		Total	2300 tons,

[1]) Chemist and Druggist **68** (1906), 20.
[2]) Report October **1892**, 41.
[3]) Report October **1904**, 81.

whilst the auctions, as a matter of fact, are reported as showing about 100 tons more, i. e. in round figures 2400 tons. The disposition was very animated, partly at decidedly higher prices. We are informed that the latter are chiefly due to competition by native purchasers, who alone have taken off the market about 800 tons, i. e. one third of the entire quantity.

Under these conditions it is keenly felt that the prices of sandalwood oil should be raised proportionate to the values of the wood, but in view of the existing competition this will no doubt remain just at present a vain desire.

The *Madras Mail* of 15th September 1905 contained a long report from the Administration of Forests in Mysore, from which we see that no fewer than 28360 sandal-trees in the Mysore district, and 973 in the Hassan district, had to be uprooted, as having been attacked by the "spike"-disease. On the other hand, detailed experiments have proved that neither inoculation with diseased shoots, nor contact of the roots of healthy and diseased trees, can transmit the disease.

The Conservator states that the disease rarely occurs in districts where the other vegetation which exists alongside the sandal-trees is strong and healthy, which would support the theory that the spike-disease depends upon the degree of nutrition, and not upon the condition of the soil, but upon the neighbouring trees which, if of less duration of life than the sandal-trees, infect the latter. For this reason the disease does not appear to be of such importance as was originally believed.

Adulterations of sandalwood oil have again been observed on several occasions. Of particular interest is the case reported upon by E. Parry[1]), as we here become acquainted with a new and rather ingeniously selected adulterant. Parry namely found in a sandal oil originating from Germany, which was at once suspected on account of its low price, an adulteration with terpineol. The oil in question had the following properties: $d_{15°}$ 0,970; α_D — 14°; esterified santalol 3,5%, apparent content of total santalol 93,5%; soluble in 5 vol. 70 per cent. alcohol.

By means of repeated fractional distillation *in vacuo* there was finally obtained a fraction consisting of about 5% of the oil used, which already by the odour revealed itself as terpineol, and which was identified as such by its physical properties and by the nitrosochloride. Parry believes that terpineol was not the only substance added, but that the oil also contained West Indian Sandalwood oil, particularly certain readily soluble fractions of the latter richer in sesquiterpene alcohol. Parry intends following this matter up further.

[1]) Chemist and Druggist **68** (1906) 72, 211.

Another case mentioned by G. Wendt[1]) deals with the use of adulterated sandal oil for the manufacture of sandal oil capsules, an occurrence to which we have repeatedly drawn attention in our last Reports[2]). The examination showed that the capsules in question contained not only an adulterated oil, but also nearly 30% less oil than was stated on the box. The manner of adulteration could not be ascertained. The manufacturer of the capsules contests the adulteration, but admitted that he had not used oil of best quality, with the explanation that only an oil had been guaranteed which would answer the requirements of the German Pharmacopœia IV, and which, as a matter of fact, the oil in question did answer.

We would add here that we have repeatedly observed, that inferior or adulterated sandalwood oils can pass the requirements of the German Pharmacopœia IV, and that it would therefore be advisable in a new edition of the Pharmacopœia at least to add the specification of the santalol content of the oil. We take this opportunity to point out once more, that in calculating the santalol content, we have taken as a basis the formula $C_{15}H_{24}O$ which according to later investigations[3]) has been recognised as more correct. In an oil with a santalol content of 90% and higher, it gives an advantage of about 1% to the older formula $C_{15}H_{26}O$.[4]). We have hitherto always made our statements in accordance with the more correct formula, and will continue to do so. Possible differences may thus be explained.

Sassafras Oil. It is well known that sassafras oil is required to be soluble in every proportion in 90 per cent. alcohol. As we have repeatedly handled oils obtained from a reliable source, which showed a slightly lower solubility, we have distilled a sassafras oil ourselves — from the root-bark of *Sassafras officinale* Nees —, in order to test the correctness of the above-mentioned requirement. We then found, in agreement with our observations made on good commercial oils, that 1 to 2 vol. 90 per cent. alcohol are necessary to dissolve 1 vol. sassafras oil, although of course it cannot be denied that there are oils which are soluble in every proportion in 90 per cent. alcohol. The remaining properties of the distillate obtained by us were: bright yellow, $d_{15°}$ 1,075, $\alpha_D + 2° 14'$; ester number 1,9. The yield of oil amounted to 3,25%.

Savin Oil. It is a well known fact that there exist considerable differences between the savin oils of German and British origin on the one hand, and the French distillate on the other, so that we have

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[1]) Pharm. Zeitg. **50** (1905), 898.
[2]) Report October **1903**, 63; October **1904**, 83; April **1905**, 72.
[3]) Comp. Report October **1900**, 58.
[4]) Comp. the table in Report April **1903**, 106.

already on a previous occasion and in another place[1]) expressed the supposition that the French oil is only met with in commerce heavily adulterated with oil of turpentine. According to Umney and Bennett[2]) this supposition does not apply to all French oils, even if they possess properties differing from those of ordinary savin oil. The differences should rather be attributed to this, that we have here to deal with distillates of two different species of Juniperus. This at least the authors have observed in an oil obtained from a very reliable source, which corresponds well with the French commercial products, whilst differing markedly from ordinary savin oil. A further examination of the plant material showed that the oil did not originate at all from the leaves of *Juniperus sabina* L, but from the very similar *Juniperus phoenicea* L. indigenous to the Mediterranean countries. The properties of this oil were as follows: $d_{15°}$ 0,892, $\alpha_D + 4° 30'$, ester content 9,3 %, content of total sabinol 17,1 %, soluble in 5 vol. 90 per cent. alcohol. The oil is therefore lighter than ordinary savin oil, further, it has but a feeble rotation, and a decidedly lower alcohol content. Contrary to the German and British[3]) distillates it is rich in low-boiling constituents, 64 % passing over up to 165°, whilst the ordinary oils do not contain such low-boiling portions at all. Of constituents may be mentioned pinene, of which the oil contains a great deal, and also cadinene, and an aldehyde which, however, occurs in the oil in such small quantity that its identification was not possible.

As, according to Umney and Bennett, it is very probable that savin oil owes its physiological action in the first place to sabinol, it follows that the oil of *Juniperus phoenicea* L. which is less rich in sabinol, must be less active than the real oil of savin, and consequently cannot be a substitute of equal value for the latter.

For the rest Umney and Bennett do not supply any proof of the identity of the alcohol contained in the oil of *Juniperus phoenicea* L. with sabinol, which was all the more necessary as the botanical relationship between the mother plants does not by any means prove that the individual constituents must be identical.

Solidago Oils. From America we received two solidago oils. The one, designated merely as "*oil of golden rod*" had a pale yellow colour and a pleasant refreshing aroma. Its specific gravity was

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[1]) Gildemeister and Hoffmann: "The Volatile Oils", pp. 274, 275.

[2]) Pharmac. Journal **75** (1905), 827.

[3]) For purposes of comparison Umney and Bennett also give the properties of a German and a British oil of savin. In this connection the exceptionally high rotation of the British oil which is said to be an authentic distillate, is worthy of note. Whilst the rotation usually fluctuates between + 42 and + 60°, the oil in question rotates + 68°. It further contains fewer high-boiling constituents than the German oil; the sabinol-content is normal.

0,8904 (15°); α_D — 15° 34′; ester number 34,2; ester number after acetylation 59,9. The oil does not form a clear solution with 10 vol. 90 per cent. alcohol, and even when 95 per cent. alcohol is used, the solution is only clear at the commencement; when more than 1,5 vol. alcohol is added, cloudiness occurs also in this case. The esters of the oil, judging from the odour, consist chiefly of bornyl acetate; from the ester number given above, a content of 12 % bornyl acetate is calculated.

We were unfortunately unable to ascertain whether the oil originates from *Solidago odora* Aiton, although this appears probable inasmuch as the distillates of this plant specially are called in America "*Oil of golden rod*".

The second sample received by us was derived froms *Solidago nemoralis*. The bright olive-green oil had a peculiar odour, reminding somewhat of cypress oil. The constants were; $d_{15°}$ 0,8799, α_D — 23° 10′, ester number 14,4, ester number after acetylation 38,2. The oil formed a cloudy solution in about 7 and more vol. 95 per cent. alcohol.

Spearmint Oil. The principal American distillers admit that with the high prices of the last few years, the consumption has fallen off, but not by far in the same proportion as the production which is said to be now only one fourth of what it used to be. For this reason a decline in the value is said to be out of the question.

In Thuringia the distillation ceased already years ago.

Spike Oil. The manufacturers in the South of France have received a useful lesson with this article. Whilst at the high tide of the lavender oil speculation as much as 12 francs were paid for spike oil, and even in October the market-price was 9,50 to 10 francs, there are now offers at 7 francs on the market, and it is very probable that we shall again arrive at normal conditions in the course of this year. In England there are large speculative stocks which are offered excitedly.

It appears advisable to refrain from large purchases until the situation has become clearer.

Star-anise Oil. Since the middle of last year the prices have advanced without interruption, and they are now about 1/- per lb. higher than at that time. The reason given, as far as Tonquin is concerned, is the bad star-anise harvest, and although no reports have been received from the neighbouring Chinese districts, the same may apply to that source of supply.

The export of Chinese oils of cassia and star-anise, according to Hong Kong export-lists, was in 1905

to the United Kingdom . . .	526 cases
„ „ Continent	2283 „
Total	2809 cases,

such a comparatively small quantity, that an error in the statistics may be assumed, inasmuch as possibly instead of cases, piculs of 2 cases are meant.

It is a well known fact that star-anise oil is obtained by distillation from the fruit of *Illicium verum,* a tree which is cultivated specially in the South of China and the North of Tonquin. In the course of researches made by Ph. Eberhardt[1]) with the view of improving the results of the cultivation, he also occupied himself whith the internal morphology of the tree, and found that the mesophyll cells of the leaves are as rich in oil as the pericarpial cells of the fruit, in which the essential oil was specially deposited. In a trial-distillation Eberhardt received from 1 kilo leaves 200 drops of an oil with a strong odour. It has a somewhat lower solidifying point than that obtained from the fruit, congealing at 13°, against the latter at 16 to 18°. In order not to interfere with the development of the trees and the blossoms, it is best to collect particularly the old leaves only once every year, in the middle of the dry season, which is the most favourable time for this purpose. The leaves are cut up small and distilled so as to obtain the oil. By making use of this new method jointly with the old one, the annual production can, if not be doubled, at least be increased by two-thirds.

Turpentine Oil. We are indebted to the kindness of Mr. W. A. Lovegrove, Deputy Conservator of Forests at Naini Tal, British India, for a sample of the Indian turpentine derived from *Pinus longifolia* Roxb. and of the oil of turpentine obtained from it, to which we have repeatedly referred in our last Reports. The products correspond in their properties with those observed by Rabak[2]). The balsam yielded on steam distillation, 19,3 % of a colourless oil, whilst a pale yellow brittle resin remained behind. The latter had the acid number 154,7, and an ester number of 8,8. The distillate behaved as follows: $d_{15°}$ 0,8741, α_D + 0° 43′, acid number 0, ester number 3,2, soluble in 7 to 8 and more vol. 90 per cent. alcohol. The oil sent to us from India had quite similar properties: $d_{15°}$ 0,8734; α_D + 3° 13′; acid number 1,9; ester number 1,3; soluble in 7,5 and more vol. 90 per cent. alcohol. In the distillation the following fractions were obtained: —

1.	165 to 170°	(747 mm.)	33 %	α_D — 3° 30′
2.	170 „ 175°	„	31 „	„ + 0° 40′
3.	175 „ 180°	„	14 „	„ + 4° 32′
4.	above 180°	„	22 „	„ + 16° 22′

[1]) Compt. rend. **142** (1906), 407.
[2]) Pharm. Review **23** (1905), 229. Report October **1905**, 68.

Although with the enormous wealth of forests of the United States of America, the question of a rapid exhaustion of the American turpentine production need not yet be considered, — in spite of the ruthless devastation of the forests by the largest and quickest possible extraction of turpentine as hitherto carried on — the American Administration of Forests has in recent years taken steps to arrest, by a careful and rational exploitation of the stock of conifers, the constantly spreading destruction of the forests. The attempts made to bring about some change in the hitherto universally applied method of collecting turpentine by the "*box*"-system for the purpose of obtaining large yields, with the view of preserving the resiniferous trees, have not remained without result. A new method, the "*cup-and-gutter*"-system, has now been proposed, which follows the lines of the system of turpentine production adopted in the South of France. A work by Charles Herty[1]), published some time ago, deals in detail with the experiments made with the above-mentioned method. But before entering more fully into this matter, we wish to return with a few words to the "*box*"-system, and briefly describe this method and its disadvantages. According to this system, the first work, when spring approaches, is to cut a groove diagonally across the trunk of the tree, inclined towards the interior and ending in a hollow about 12″ or 18″ above the level of the ground. Now when with the warmer weather the sap of the tree begins to flow, the bark at both sides of the "box" or reservoir for the resin is peeled off up to a height of 8″, in strips about 2″ wide. The space between the box and the peeled-off strips is now deprived of its bark down to the splint, and shortly afterwards the sap commences to flow down into the "box". This work is continued every 2 or 3 weeks up to the end of October, and has the effect of constantly opening up fresh passages for the resin, which secrete their contents slowly into the "box". With the advent of the colder weather the secretion of resin becomes less and finally ceases completely. After 4 or 5 years the same tree is no longer tapped. As already indicated, this "*box*"-system has many drawbacks, due both to the manner of obtaining the resin, and to the destruction of the tree by other influences. The cutting of the hollow causes the destruction of numerous resin-passages, and much resin is consequently lost. Moreover, the quality of the resin suffers from the fact that the readily-volatile portions of the sap of the tree evaporate, as they have to travel along a constantly increasing distance, owing to the cutting away being continued in an upward direction.

The new method which may be considered a combination of the "*box*"-system and the method generally employed in France, does

[1]) Dr. Charles Herty, A new method of turpentine orcharding; Washington, 1903.

away with most of the drawbacks mentioned above. In the first place, the cutting of a large hollow in the trunk is obviated. Its place is taken by a receptacle which is suspended from a nail in the trunk. As in the "*box*"-system, here also the first work is cutting strips in the bark and the splint, and as the work proceeds the space above the receptacle is gradually cleared of bark. In order to let the exuding resin collect in the earthenware pots or vessels placed below, two strips or gutters of galvanised sheet iron about 2″ wide by 6″ to 12″ long are employed. These are placed in grooves cut into the trunk with a broad axe in such manner, that each of the two cuts forms an angle of 60° with the longitudinal axis of the tree, and the two together therefore form an angle of 120° open at the top. The two gutters however are not placed at the same height, but one about 1″ or 2″ above the other, so that the resin flowing along the upper gutter only passes the other one when flowing down, and then passing through the lower gutter reaches the vessel placed below the latter. When the cuts in the trunk and the peeling of the bark is continued in an upward direction, the gutters and the vessel are also moved upwards. In stouter trees containing more resin, several such vessels can of course be placed around the tree. The new method is still being tried further, but it can be foreseen that it guarantees a more rational output of the trees than is possible with the "*box*"-system.

Utz[1]) makes some further communications on the examination of oil of turpentine and substitutes of oil of turpentine. He determined the iodine number[2]) of various turpentine oils and pine tar oils, and found somewhat considerable differences in the values; he draws the conclusion that the iodine number has little importance for the analysis of turpentine oil, as according to experiments made, the iodine numbers vary considerably according to the manner of keeping the oils. Utz has confirmed the colour reaction indicated by Valenta for pinolin. He also found that pinolin, in the treatment with concentrated and fuming sulphuric acid, shows a larger separation than the different turpentine oils, whilst the refraction of the oil separated off is lower than that of oil of turpentine.

Vaubel[3]) recommends for the valuation of turpentine oils, the determination of the bromine number, which the author accomplishes

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[1]) Chem. Rev. Fett- und Harzindustrie **12** (1905), 231. Accord. to Chem. Centralbl. **1905**, II, 1393,

[2]) The iodine numbers ascertained by Utz for turpentine oil (223,5 to 331,6) lie between the values found earlier by Worstall on the one hand, and by Harvey on the other, and they afford a fresh proof of how much depends here on the conditions of the test. Comp. Report October **1904**, 85.

[3]) According to a paper. Zeitschr. f. öff. Chem. **11** (1905), 429. Acc. to Chem. Centralbl. **1906**, I. 199.

as follows: 1 to 2 grams oil are dissolved in 100 cc. glacial acetic acid, or better chloroform[1]), 5 g. potassium bromide and 20 cc. fuming hydrochloric acid are added, and next enough of a titrated solution of potassium bromate to cause a permanent bromine reaction. The bromine numbers found by Vaubel agree well with the iodine numbers found by Worstall. On the other hand, Holde considers the specific gravity of the turpentine oils, and Herzfeld their behaviour towards concentrated and fuming sulphuric acid, as better standards for valueing than the bromine number.

Wintergreen Oil. The last shipments made by our New York branch have still been invoiced at the old price, but for future consignments the prospects are higher prices. As the present value is abnormally low, the timely purchase of supplies should not be delayed.

Siro Grimaldi[2]) has detected salicylic acid (which most probably originates from the action of a ferment on a glucoside as methyl ester of salicylic acid) in various parts of plants, as for example in the agriots which in each kilogr. fruit contains 0,1 to at most 0,45 to 0,5 mg. salicylic acid; further in the berries of *Vitis labrusca* Linn. and in those of *Rubus idaeus* Linn., especially in the raspberries of Monte Amiata. The author detected this acid in the benzene or ether extract of the parts of the plant in question, by means of the ferric chloride reaction, and by conversion of the acid into ammonium picrate when submitted to the action of aqueous nitric acid and subsequently of ammonia.

Wormwood Oil. Over-production in the South of France and Algeria has depressed the prices as never before, whilst there is an excellent selection of qualities. The competition of the American oil has been paralysed by the abnormal state of the price.

Ylang-Ylang Oil. Although the consignments of the "Sartorius" brand were again more abundant last year, the demand could only be met with great difficulty. According to the most recent reports from Manila, dating from the end of January, there was then a scarcity of blossoms, and the distillation had been interrupted in consequence; but this is now probably past, as a shipment has meanwhile been advised by cable. Our friends in Manila make every possible effort to increase the production to such an extent, that the consumption can always be fully satisfied. According to official consular reports, the value of ylang-ylang oil exported from Manila in the year 1904/1905 amounted to 100349 dollars, i. e. about 300 dollars less than in the two preceding years.

[1]) Comp. also Pharm. Ztg. **51** (1906), 257.

[2]) Staz. sperim. agrar. ital. **38** (1905), 28 to 21. Accord. to Chem. Centralbl. **1905**, II., 1503.

Novelties.

Some new oils obtained from the Imperial Biologico-Agricultural Institute of Amani (German East Africa) have been examined by R. Schmidt and K. Weilinger[1]).

Oil from the bark of *Ocotea usambarensis* Engl. The bark of this tree which belongs to the Lauraceæ and which is found in fairly large numbers in the primeval forests, yielded 0,15 % essential oil of the following properties: boiling point at 10 mm. pressure 50 to 160°, $d_{20°}$ 0,913, n_D 1,476, $\alpha_{D20°}$ — 11° 12′, acid number 1,2, ester number 12,5; content of free alcohols ($C_{10}H_{18}O$) 4,5 %; free from sulphur and nitrogen. By shaking the oil with potash liquor, 0,3 % of a phenol not further identified were obtained, and by means of bisulphite liquor 1 % myristinic aldehyde which was identified by its semicarbazone (melting point 100 to 101°) and by oxidation into myristinic acid. When the oil was shaken with hydrazin benzene sulphoacid, a very small quantity of a ketone was obtained, whose semicarbazone melted at 197°. The oil further contained 40 % cineol (identified by the iodol compound), 40 % l-terpineol (boiling point 100 to 110° at 12 mm. pressure; $d_{20°}$ 0,922; n_D 1,484; α_D — 37° 6′) which was detected by conversion into dipentene dihydrochloride (melting point 46°), and 10 % sesquiterpene $C_{15}H_{24}$ (boiling point 136 to 142° at 12 mm pressure: $d_{20°}$ 0,915, n_D 1,535; α_D + 7° 46′), whose dihydrochloride (melting point 116 to 117°) is not identical with cadinene hydrochloride.

Oil of *Piper Volkensii* C. D. C. The leaves of this plant which is found in considerable numbers in the damp forests of Usambara, yielded 0,3 % essential oil of a bright-brown colour, and a powerful pleasant odour, which had the following properties: boiling point 90 to 175° at 12 mm. pressure, $d_{20°}$ 0,934, n_D 1,5017, α_D — 8° 24′, ester-content 6 % geranyl acetate, content of free alcohols 14 % $C_{10}H_{18}O$. By means of phthalic acid anhydride there were abstracted from the oil 4 % of a primary alcohol (possibly citronellol). The principal fraction (70 %) of the saponified oil boiled at 135° to 148°, at 15 mm. pressure, and absorbed bromine with formation of a bromide $C_{11}H_{12}O_3Br_2$ (melting point 122°), which was reconverted into the body $C_{11}H_{12}O_3$ by reduction with zinc dust and glacial acetic acid. As this product contains 14,1 % methoxyl, the authors believe that they may possibly have to deal with a methoxylized safrol. In addition to this, they detected in the principal fraction the sesquiterpene limene found by Burgess and Page in oil of

[1]) Berl. Berichte **39** (1906), 652.

limette. Like the latter, the sesquiterpene found absorbs 3 molecules hydrochloric acid (melting point of the hydrochloride 79 to 80°) and 6 atoms bromine (melting point of the bromide 154°).

New Pharmacopœias.

In our last Report we have already published a summary of the requirements specified by the new American Pharmacopœia for the essential oils admitted to it, and we stated at the same time that a discussion of the details was at that moment not possible, but would follow in the present Report. In the meantime, two more new Pharmacopœias have appeared, namely the seventh edition of the Spanish Pharmacopœia which has recently come into force, and the eighth edition of the Austrian Pharmacopœia which takes effect from the 1st July 1906. As on previous occasions, we will in the following pages briefly quote the requirements specified in the various Pharmacopœias for the essential oils, and in each case discuss whatever may need supplementing or correcting, as that will be the best way of preventing any misunderstandings which might arise in judging individual oils on the basis of the Pharmacopœia in question.

The new (IV.) Dutch Pharmacopœia unfortunately only reached us after the editorial portion of this Report was closed, and we therefore reserve a discussion of same for the next October Report.

American Pharmacopœia.

(The Pharmacopœia of the United States of America, 8th decennial revision).

The new edition of the American Pharmacopœia has deservedly met with general approbation. There are everywhere evidences of a serious effort to make the widest possible use of the achievements of Science; particularly this is the case in the directions for testing. This also applies especially to the essential oils, which are mostly described in detail in such manner that the American Pharmacopœia may in this respect be characterized to a certain extent as typical. This favourable opinion of the whole does not preclude that some statements made in the Pharmacopœia are not correct, and also that several directions for testing call for criticism. For the sake of expediency, we will first of all discuss in a connected form, the specific gravities specified by the Pharmacopœia, and then deal with the oils themselves.

As already mentioned by us in our Report of October 1905, p. 74, the new American Pharmacopœia does not indicate the specific

gravities of the essential oils, as is usually done, at $\frac{15°}{15°}$, but at $\frac{25°}{25°}$. This rule has induced us to determine for all essential oils included in the Pharmacopœia, the differences existing between the specific gravities at $\frac{15°}{15°}$ and at $\frac{25°}{25°}$, so as to form an opinion whether and in how far the limits of value given in the Pharmacopœia agree with those obtained at 15°. We have here in several cases found more or less considerable differences. For the purpose of a better review, we have combined the results obtained in a tabulated form (p. 71). The limits of value given in the American Pharmacopœia, which do not agree with ours, are printed in heavy type. These limits printed thus cannot and should not in our opinion be accepted as such, for they are inconsistent with the values fixed for 15°, and are consequently incorrect. Differences of 1 in the third decimal figure have been left out of account, as they lie within the limits of error. We would still mention that the differences between the specific gravities determined at $\frac{15°}{15°}$ and at $\frac{25°}{25°}$, as given by us, agree well on the whole with those ascertained previously by Schreiner and Downer[1]), and also that the average value of these differences is the same as that found by those authors, viz. 0,00064 per degree of temperature.

Of alcohols, the American Pharmacopœia recognises a strong alcohol of 94,9 per cent. by volume (Alcohol), and a weak one of 48,9 per cent. by volume (Alcohol dilutum). In the following pages the former is designated simply as "alcohol."

Anise Oil (*Oleum anisi*). Colourless or faintly yellow: $d_{25°}$ 0,975 to 0,985[1]); $\alpha_{D\,25°}$ — 2°[2]); solidifying point not below + 15°; soluble in an equal volume alcohol and in 5 vol. 90 per cent. alcohol.

[1]) The upper limit of value should be 0,988, as otherwise especially the oils richest in anethol, and consequently the most valuable anise oils, could not be used. Comp. also the table (p. 71).

[2]) This should read: up to — 2°.

Benzaldehyde (*Benzaldehydum*). Colourless liquid, strongly refractive, with at least 85% pure benzaldehyde[1]); $d_{25°}$ about 1,045; $\alpha_D \pm 0°$; boiling point 179 to 180°; soluble in alcohol in every proportion; test for absence of chlorinated products.

[1]) According to the method of determination by means of neutral sodium sulphite indicated by the Pharmacopœia, we found it impossible to obtain even approximately satisfactory results; for this reason, we greatly doubt the usefulness of this method.

Bitter Almond Oil (*Oleum amygdalæ amaræ*). Colourless or yellow; content of benzaldehyde at least 85%[1]); content of hydrocyanic acid between 2 and 4%[2]); $d_{25°}$ 1,045 to 1,060[3]); $\alpha_D \pm 0°$[4]);

[1]) Pharm. Archives **4** (1901), 165. Report April **1902**, 80.

Table.

	$d\frac{15°}{15°}$	$d\frac{25°}{25°}$	Difference	Limits of value at $\frac{15°}{15°}$	Limits of value at $\frac{25°}{25°}$	American Pharmacopœia $\frac{25°}{25°}$
Anise Oil	0,9915	0,9855	0,0060	0,984—0,994	0,978—0,988	0,975—**0,985**
Benzaldehyde . . .	1,0584	1,0515	0,0069	1,050—1,055	1,043—1,048	about 1,045
Bitter Almond Oil .	1,0655	1,0587	0,0068	1,045—1,070	1,038—1,063	**1,045—1,060**
Cajeput Oil	0,9215	0,9151	0,0064	0,919—0,930	0,913—0,924	**0,915**—0,925
Caraway Oil	0,9080	0,9023	0,0057	0,905—0,915	0,899—0,909	**0,905**—0,915
Cassia Oil, rect. . .	1,0551	1,0489	0,0062	1,053—1,065	1,047—1,059	1,045—**1,055**
Chenopodium Oil .	0,9769	0,9706	0,0063	?		0,965—0,985
Cinnamic Aldehyde	1,0560	1,0504	0,0056	1,054—1,058	1,048—1,052	about **1,047**
Clove Oil	1,0487	1,0422	0,0065	1,040—1,060	1,033—1,053	**1,040**—1,060
Copaiba Oil	0,9056	0,9002	0,0054	0,900—0,920	0,895—0,915	0,895—**0,905**
Coriander Oil . . .	0,8739	0,8672	0,0067	0,870—0,880	0,863—0,873	0,863—0,878
Cubeb Oil	0,9214	0,9159	0,0055	0,915—0,930	0,909—0,924	0,905—0,925
Erigeron Oil	0,8865	0,8803	0,0062	0,850—0,870	0,844—0,864	0,845—0,865
Eucalyptol	0,9294	0,9227	0,0067	0,928—0,930	0,921—0,923	**0,925**
Eucalyptus Oil . . .	0,9146	9,9083	0,0063	0,910—0,930	0,904—0,924	0,905—0,925
Eugenol	1,0716	1,0650	0,0066	1,071—1,074	1,064—1,067	**1,072**—1,074
Fennel Oil	0,9715	0,9653	0,0062	0,965—0,977	0,959—0,971	0,953—0,973
Hedeoma Oil (Oil of Amer. Pennyroyal)	0,9331	0,9271	0,0060	0,925—0,940	0,919—0,934	0,920—0,935
Oil of Juniper berries	0,8655	0,8593	0,0062	0.860—0,885	0,854—0,879	**0,860**—0,880
Lavender Oil	0,8864	0,8797	0,0067	0,882—0,895	0,875—0,888	**0,880**—0,892
Lemon Oil	0,8585	0,8527	0,0058	0,857—0,861	0,851—0,855	0,851—0,855
Mustard Oil	1,0200	1,0120	0,0080	1,016—1,025	1,008—1,017	**1,013**—1,020
Nutmeg Oil	0,9037	0,8972	0,0065	0,870—0,930	0,864—0,924	0,862—**0,910**
Peppermint Oil . .	0,9060	0,9006	0,0054	0,900—0,920	0,895—0,915	0,894—0,914
Pimenta Oil	1,0440	1,0372	0,0068	1,025—1,055	1,018—1,048	**1,033**—1,048
Rose Oil[1])		0,8625			0,854—0,867	0,855—**0,865**
Rosemary Oil . . .	0,9077	0,9011	0,0066	0,900—0,920	0,893—0,913	0,894—0,912
Safrol	1,1054	1,0985	0,0069	1,105—1,107	1,098—1,100	**1,105**—1,106
Sandalwood Oil . .	0,9782	0,9735	0,0047	0,975—0,985	0,970—0,980	0,965—**0,975**
Sassafras Oil	1,0807	1,0740	0,0067	1,070—1,082	1,063—1,075	**1,065**—1,075
Savin Oil	0,9208	0,9150	0,0058	0,910—0,930	0,904—0,924	0,903—0,923
Spearmint Oil . . .	0,9352	0,9290	0,0062	0,920—0.940	0,914—0,934	0,914—0,934
Sweet Orange Oil .	0,8509	0,8452	0,0057	0,849—0,853	0,843—0,847	0,842—0,846
Thyme Oil, white .	0,9068	0,9007	0,0061	0,900—0,935	0,894—0,929	**0,900**—0,930
Turpentine Oil . . .	0,8682	0,8616	0,0066	0,865—0,875	0,858—0,868	**0,860**—0,870
Turpentine Oil, rect.	0,8708	0,8643	0,0065	0,860—0,871	0,853—0,864	**0,860**—0,865
Wintergreen Oil:						
a) from *Betula lenta* L.	1,1870	1,1794	0,0076	1,180—1,188	1,172—1,180	1,172—1,180
b) from *Gaultheria procumbens* L.	1,1864	1,1788	0,0076	1,180—1,188	1,172—1,180	1,172—1,180
c) artificial	1,1896	1,1817	0,0079	1,185—1,190	1,177—1,182	**1,180**—1,185

[1]) The limits of value given for rose oil were based upon those in force for $\frac{30°}{15°}$.

boiling point about 180°; soluble in every proportion in alcohol, also in an equal volume 70 per cent. alcohol[5]); test for absence of chlorinated products.

[1]) Comp. note under benzaldehyde.

[2]) Such a content of hydrocyanic acid cannot always be guaranteed.

[3]) The specific gravity given is for a temperature of 15°, but it should be taken into consideration that even in the case of absolutely normal oils, it often amounts to 1,070; for 25° the following figures apply: 1,038 to 1,063 (comp. table).

[4]) Occasionally a feeble optical activity is also observed.

[5]) Of 70 per cent. alcohol, 1 to 2 volumes are required to dissolve the oil.

Cajeput Oil (*Oleum cajuputi*). Colourless or greenish; cineol-content at least 55 per cent. by volume[1]); $d_{25°}$ 0,915 to 0,925[2]); laevorotatory, $\alpha_{D25°}$ not above — 2°[3]); soluble in every proportion in alcohol, also in 1 part 80 per cent. alcohol.

[1]) The estimation of cineol is accomplished by means of phosphoric acid in the following manner: 10 cc. oil are dissolved in 50 cc. petroleum ether, and to the well cooled solution (freezing mixture) is gradually added, whilst stirring, concentrated phosphoric acid, until the white compound separating off acquires a yellowish (or reddish) shade. The crystalline mass is then filtered off with a suction pump, washed with petroleum ether, pressed to remove the last liquid portions, and decomposed with water. The cineol separated off is estimated volumetrically and the percentage calculated.

We have again convinced ourselves by estimations of mixtures of a known cineol-content, that this method does not always give reliable results. This applies specially to oils less rich in cineol; for example, in mixtures of 50 per cent., the content of cineol found was up to 8 per cent. too little, although we endeavoured by different small improvements, to avoid sources of error as much as possible. For this reason, the cineol-estimations can only lay claim to approximate accuracy.

[2]) As lower limit of value, 0,913 is to be recommended (comp. table).

[3]) With pure distillates, we have observed rotations up to — 2° 40′.

Camphor (*Camphora*). White, transparent mass; $d_{25°}$ 0,990; α_D to the right; melting point 175°; boiling point 204°.

Caraway Oil (*Oleum cari*). Colourless or pale yellow; $d_{25°}$ 0,905 to 0,915[1]); $\alpha_{D25°}$ + 70 to + 80°; soluble in an equal volume alcohol, and in 3 to 10 volumes 80 per cent. alcohol.

[1]) The specific gravity given applies to a temperature of 15°; it should read: $d_{25°}$ 0,899 to 0,909 (comp. table).

Cassia Oil[1]) (*Oleum cinnamomi*). Yellowish or brownish; content of cinnamic aldehyde at least 75 per cent. by volume; $d_{25°}$ 1,045 to 1,055[2]); $\alpha_{25°}$ between — 1° and + 1°; soluble in 2 volumes 70 per cent. alcohol.

[1]) Only the rectified oil answers the requirements given.

[2]) The upper limit of value given is slightly too low; it should be 1,059 (comp. table).

Chenopodium Oil (*Oleum chenopodii*). Colourless or yellow, $d_{25°}$ about 0,965 to 0,985[1]); lævorotatory, $\alpha_{D25°}$ not above — 5°[2]); soluble in 5 volumes 70 per cent. alcohol.

[1]) The Pharmacopœia here quite correctly only requires approximate values, as oil of chenopodium is extremely variable owing to its content of a constituent which decomposes very readily; this also causes changes in the specific gravity.

[2]) We have observed with good commercial oils, rotations up to — 6°.

Cinnamic aldehyde (*Cinnaldehydum*). Colourless[1]); containing at least 95% pure cinnamic aldehyde; $d_{25°}$ about 1,047[2]); $\alpha_D \pm 0°$; boils about 250° with decomposition; solidifies in a freezing mixture and melts again at — 7,5°; soluble in every proportion in alcohol.

[1]) Cinnamic aldehyde is not colourless, but bright yellow.

[2]) The statement of the specific gravity is not correct, it should read: $d_{25°}$ 1,048 to 1,052 (comp. table).

Clove Oil (*Oleum caryophylli*). Colourless or pale yellow; eugenol-content at least 80 per cent. by volume; $d_{25°}$ 1,040 to 1,060[1]); soluble in an equal volume alcohol, and in about 2 volumes 70 per cent. alcohol.

[1]) As oils with a eugenol-content down to 80% are admitted, the lower limit of the specific gravity should be reduced to 1,033 (comp. table).

Copaiba Oil (*Oleum copaibæ*). Colourless or pale yellow, $d_{25°}$ 0,895 to 0,905[1]); α_D to the left; soluble in 2 vol. alcohol[2]).

[1]) The specific gravity at 15° amounts to up to 0,918, as we have recently observed with one of our own distillates (comp. Report April **1905**, 25). The specific gravity mentioned corresponds to the value 0,915 at 25° (see table).

[2]) On the strength of observations with authentic material we are in a position to state that 1 vol. copaiba oil requires 5 to 10 vol. 95 per cent. alcohol to form a solution. See Report April **1905**, 25.

Coriander Oil (*Oleum coriandri*). Colourless or faintly yellow; $d_{25°}$ 0,863 to 0,878; $\alpha_{D25°}$ + 7 to + 14°; soluble in 3 volumes 70 per cent. alcohol; in 80 and 90 per cent. alcohol soluble in every proportion.

Oil of Cubebs (*Oleum cubebæ*). Colourless, pale green, or yellow; $d_{25°}$ 0,905 to 0,925; $\alpha_{D25°}$ — 25 to — 40°.

Erigeron Oil (*Oleum erigerontis*). Faintly yellow; $d_{25°}$ 0,845 to 0,865; $\alpha_{D25°}$ about + 50°; soluble in an equal volume alcohol.

Eucalyptol. Colourless; $d_{25°}$ 0.925[1]); $\alpha_D \pm 0°$; boiling point 176 to 177°; solidifies on cooling into needle-shaped crystals, which melt at — 1°; soluble in every proportion in alcohol.

[1]) The specific gravity at 25° is not 0,925, but fluctuates between 0,921 and 0,923 (comp. table).

[2]) Solidification has to be started in case of need by rubbing a glass rod on the wall of the vessel.

Eucalyptus Oil (*Oleum eucalypti*). Colourless or faintly yellow[1]); cineol-content at least 50 per cent. by volume[2]); $d_{25°}$ 0,905 to 0,925; α_D 25° not above + 10°; soluble in every proportion in alcohol and in 3 volumes 70 per cent. alcohol; free from phellandrene.

[1]) The oil has occasionally also a greenish shade.

[2]) With regard to the cineol-estimation, compare what has been said under cajeput oil.

Eugenol. Colourless or faintly yellow: $d_{25°}$ 1,072 to 1,074[1]); $\alpha_D \pm 0°$; boiling point 251 to 253°; soluble in every proportion in alcohol, and in 2 parts 70 per cent. alcohol.

[1]) These figures apply to 15°; at 25° the specific gravity lies between 1,064 and 1,067 (comp. table).

Fennel Oil (*Oleum fœniculi*). Colourless or faintly yellow; $d_{25°}$ 0,953 to 0,973; solidification point not below + 5°[1]); soluble in an equal volume alcohol, likewise in 10 volumes or less 80 per cent. alcohol.

[1]) Solidification must in case of need be introduced by inoculation with a small crystal of anethol. The lowest limit of the solidification point might suitably be + 4°, as in commercial products it is usually found between + 4 and + 6°.

Oil of Hedeoma or **American pennyroyal** (*Oleum hedeomæ*). Faintly yellow: $d_{25°}$ 0,925 to 0,935; α_D 25° from about + 18 to + 22°; soluble in 2 and more vol. 70 per cent. alcohol.

Oil of Juniper berries (*Oleum juniperi*). Colourless, faintly green or yellow; $d_{25°}$ 0,860 to 0,880[1]); soluble in 10 volumes 90 per cent. alcohol[2]).

[1]) Oil of juniper berries is also frequently lighter; a lowest limit of 0,854 would be more suitable (comp. table).

[2]) The specification of solubility is mostly only answered by quite fresh distillates; even when kept in a rational manner the solubility of oil of juniper berries diminishes rapidly.

Lavender Oil (*Oleum lavandulæ florum*). Colourless or yellow; $d_{25°}$ 0,880 to 0,892[1]); soluble in 3 vol. 70 per cent. alcohol.

[1]) The lower limit of the specific gravity is not correct; it should read: 0,875 (comp. table).

Lemon Oil (*Oleum limonis*). Faintly yellow, citral-content not less than 4 %[1]); $d_{25°}$ 0,851 to 0,855; $\alpha_{D25°}$ not below + 60°[2]); α_D of the first 10 % of the distillate may only differ 2° from the angle of rotation of the oil[3]).

[1]) The citral-determination is made by Sadtler's method (comp. Reports April **1904**, 47 and October **1904**, 119) with this extension, that in addition to the actual test also a "blind" test without oil is made; this is no doubt a decided step in advance as in this manner the end of the reaction can be observed or approximated somewhat better, but in the tests made by us we have again come to the conclusion, that a really exact determination is not possible even in this manner, and for this reason we must continue, as before, to characterize the method as unreliable.

[2]) The rotation of lemon oil varies considerably with the temperature; the one given above would correspond to a rotation of 60° 41′ at the usual observation temperature of 20°. As pure oils are frequently met with, with a rotation down to 58°, and as most oils rotate about 60°, the above requirement of the Pharmacopœia does not take the actual facts sufficiently into account.

[3]) According to our experience, the difference in pure oils frequently amounts to up to 5°.

Menthol. Colourless needle-shaped or prismatic crystals; melting point 43°; boiling point 212°; alcoholic solution neutral and lævorotatory.

Mustard Oil (*Oleum sinapis volatile*). Colourless or faintly yellow; $d_{25°}$ 1,013 to 1,020[1]); boiling point 148 to 152°; lowest content of allyl isothiocyanate 92 %[2]); soluble in every proportion in alcohol.

[1]) The lower limit is given too high, and should be 1,008 (comp. table).
[2]) With regard to the determination, comp. the present Report p. 45.

Nutmeg Oil (*Oleum myristicæ*). Colourless or faintly yellow; $d_{25°}$ 0,862 to 0,910[1]); $\alpha_{D25°}$ + 14 to + 28°[2]); soluble in an equal vol. alcohol, and in 3 vol. 90 per cent. alcohol. When 2 to 3 cc. oil are evaporated, no crystallising residue should remain behind.

[1]) The upper limit is given too low and must be increased to 0,924, as otherwise just the oil from the best material is excluded from medicinal use. Comp. Report October **1904**, 65; see also table.
[2]) We have observed in our own distillates from nutmeg of best quality, rotations down to + 7° 52′. Comp. Report October **1904**, 65.

Peppermint Oil[1]) (*Oleum menthæ piperitæ*). Colourless[2]); $d_{25°}$ 0,894 to 0,914; $\alpha_{D25°}$ — 25 to — 33°; ester (menthyl acetate) at least 8 %[3]); total menthol (free and esterified) at least 50 %; soluble in an equal vol. alcohol; the solution in 4 volumes 70 per cent. alcohol may at most show a feeble opalescence.

[1]) The requirements given for peppermint oil are partly contradictory, so that it is not clear whether the oil from the State of New York ("Wayne County Oil") or that from Michigan ("Western Oil") is to be the official oil. Whereas the rotation applies chiefly to the first-named oil (Michigan oil rotates between — 18 and — 29°), the requirements of solubility exclude the former as the New York oil is not soluble in 70 per cent. alcohol. It is difficult to understand why both oils are not admitted.
[2]) Peppermint oil is not always colourless, but sometimes yellowish or greenish yellow.
[3]) The ester-content is frequently lower; we have observed in authentic oils down to 4 %.

Pimenta Oil (*Oleum pimentæ*). Colourless, yellow, or reddish; eugenol-content at least 65 per cent. by volume; $d_{25°}$ 1,033 to 1,048[1]); soluble in every proportion in 90 per cent. alcohol and also in 2 vol. 70 per cent. alcohol.

[1]) The lower limit of value is given too high, and should be 1,018. Comp. table; see also German Report April **1899**, 39.

Rose Oil (*Oleum rosæ*). Faintly yellow; $d_{25°}$ 0,855 to 0,865[1]); saponification number 10 to 17[2]); solidifying point between 18 and 22°[3]).

[1]) The upper limit is given too low, and should be 0,867 (comp. table).
[2]) We have observed in pure oils saponification numbers betwen 8,5 and 19.
[3]) As upper limit for the solidifying point 23.5° might be recommended.

Rosemary Oil (*Oleum rosmarini*). Colourless or faintly yellow; $d_{25°}$ 0,894 to 0,912; $\alpha_{D25°}$ not above + 15°; the first 10% of the distillate must also be dextrorotatory. Ester-content (calculated as bornyl acetate) at least 5%; total borneol at least 15%[1]); soluble in 0,5 and more vol. 90 per cent. alcohol, and also in 2 to 10 vol. 80 per cent. alcohol.

[1]) These requirements cannot be upheld; we have observed in good oils an ester-content down to 1,2%, and a total content of borneol down to about 10%.

Safrol (*Safrolum*). Colourless or faintly yellow; $d_{25°}$ 1,105 to 1,106[1]); α_D ± 0°; boiling point about 233°; when cooled to — 20° or below, is solidifies into a crystalline mass which does not melt below + 11°; soluble in about an equal volume alcohol, and in about 30 volumes 70 per cent. alcohol.

[1]) The *data* of the specific gravity approximately correspond to those determined for 15°: 1,105 to 1,107; at 25° the specific gravity varies between 1,098 and 1,100 (comp. table).

Sandalwood Oil, East Indian (*Oleum santali*). Faintly yellow; $d_{25°}$ 0,965 to 0,975[1]); $\alpha_{D25°}$ — 16 to — 20°; santalol-content not below 90%[2]); soluble in 5 vol. 70 per cent. alcohol.

[1]) The upper limit of value is too low, it should be 0,980 (comp. table).

[2]) It is to be regretted that the Pharmacopœia bases its calculation of santalol on the formula $C_{15}H_{26}O$. We have already repeatedly pointed out that according to recent investigations the formula $C_{15}H_{24}O$ is undoubtedly more correct. Comp. Report October **1900**, 58, and the present Report p. 60. The lowest content of 90% mentioned above, and based upon $C_{15}H_{26}O$, corresponds to a minimum of 89,2% calculated on $C_{15}H_{24}O$.

Sassafras Oil (*Oleum sassafras*). Yellow or reddish yellow; $d_{25°}$ 1,065 to 1,075[1]); $\alpha_{D25°}$ not above + 4°; soluble in every proportion in 90 per cent. alcohol[2]).

[1]) For the lower limit of value, 1,063 is more suitable (comp. table).

[2]) Not every oil answers this requirement. We have again recently found in one of our own distillates, that 1 to 2 vol. 90 per cent. alcohol are required to dissolve 1 vol. sassafras oil; this observation agrees with those repeatedly made with good commercial oils. Comp. also the present Report p. 61.

Savin Oil (*Oleum sabinæ*). Colourless or yellowish; $d_{25°}$ 0,903 to 0,923; $\alpha_{D25°}$ + 40 to + 60°; soluble in about 0,5 volumes and more 90 per cent. alcohol.

Spearmint Oil (*Oleum menthæ viridis*). Colourless, yellow, or greenish yellow; $d_{25°}$ 0,914 to 0,934; $\alpha_{D25°}$ — 35 to — 48°; with an equal volume 80 per cent. alcohol it forms a clear solution which becomes cloudy when further diluted.

Sweet Orange Oil (*Oleum aurantii corticis*). Faintly yellow[1]); $d_{25°}$ 0,842 to 0,846; $\alpha_{D25°}$ not below + 95°[2]).

[1]) The colour of orange oil is yellow to yellow-brown.

[2]) Calculated for 20°, the rotation is + 96°; we have observed as lowest value at 20° + 95° 30′.

Thyme Oil *(Oleum thymi)*. Colourless[1]); $d_{25°}$ 0,900 to 0,930[2]); feeble lævorotation, $\alpha_{D25°}$ not above — 3°[3]); phenol-content a least 20 per cent. by volume; soluble in 0,5 vol. alcohol and in 1 to 2 vol. 80 per cent. alcohol.

[1]) The rectified oils also frequently acquire again the red-brown colour of the crude oil.

[2]) 0,900 is too high as lowest limit of value, and this should be 0,894 (comp. table).

[3]) We have also repeatedly observed oils with a feeble dextrorotation; further, the rotation is sometimes a little higher than indicated in the Pharmacopœia. In most cases, the optical behaviour of the oil can only be determined approximately on account of the dark colour.

Thymol. Large colourless, transparent rhombic prisms; $d_{25°}$ 1,030; melting point 50 to 51°; the alcoholic solution is optically inactive.

Turpentine Oil *(Oleum terebinthinæ)*. Colourless; $d_{25°}$ 0,860 to 0,870[1]); on distillation the bulk should pass over between 155 and 162°; soluble in 3 vol. alcohol.

[1]) It would be more correct to fix 0,858 as the lowest limit of value (comp. table).

Turpentine Oil, rectified *(Oleum terebinthinæ rectificatum)*. Colourless; $d_{25°}$ 0,860 to 0,865[1]),

[1]) The lower limit applies to a temperature of 15°; for 25° it is 0,853 (comp. table).

Vanillin. Fine, white, crystalline needles; soluble in about 100 parts water of 25°, and in 15 parts of 80°; readily soluble in alcohol; melting point 80 to 81°.

Wintergreen Oil:

a) **from Betula lenta L.** *(Oleum betulæ)*. $\alpha_D \pm 0°$; for the rest, the same properties as *Oleum gaultheriæ*.

b) **from Gaultheria procumbens L.** *(Oleum gaultheriæ)*. Colourless or almost colourless[1]); $d_{25°}$ 1,172 to 1,180; feeble lævorotation, $\alpha_{D25°}$ up to — 1°; boiling point 218 to 221°.

[1]) The oils are frequently of a reddish colour, owing to traces of iron.

c) **Artificial Wintergreen Oil** *(Methylis salicylas)*. Colourless; $d_{25°}$ 1,180 to 1,185[1]); $\alpha_D \pm 0°$; boiling point 219 to 221°; soluble in every proportion in alcohol.

[1]) The lower limit is given too high; it should be 1,177 (comp. table).

Austrian Pharmacopœia.

(Pharmacopœia Austriaca ed. VIII).

Owing to the many incorrect statements regarding essential oils contained in the seventh Edition of the Austrian Pharmacopœia, the eighth Edition just issued is all the more welcome, as the defects

mentioned above have been put right in almost every case, and the requirements specified may, whith a few exceptions which still stand in need of correction, be characterised as answering the purpose and up to date. Following the example of other Pharmacopœias, the editors of the Austrian have also endeavoured to replace essential oils wherever possible by their active constituents, as for instance anise oil by anethol, clove oil by eugenol, etc. There has further been added cajeput oil, whilst bergamot oil is now no longer included.

Where "parts" are mentioned, they are parts by weight.

The alcohols coming under consideration are the following:

a) Spiritus (Spiritus vini concentratus) with 90 to 91,2 per cent. by volume, and

b) Spiritus dilutus (Spiritus vini dilutus) with 68 to 69 per cent. by volume.

Anethol (*Anetholum*). Prepared from anise oil[1]). White crystalline mass; d 0,984 to 0,986[2]); melting point 20 to 21°[3]); boiling point 232 to 234°; soluble in 2 parts Spiritus[4]); volatile when heat is applied, without leaving any (or only a small) residue.

[1]) It is no doubt generally known that fennel oil and star-anise oil are also crude materials for anethol. The anethol is of course the same in every case.

[2]) The specific gravity is for 25°.

[3]) The melting point of pure anethol lies between 22 and 23°, the solidifying point between 21 and 22°.

[4]) 2 to 3 volumes alcohol of 90 per cent. by vol. are required to dissolve 1 vol. anethol.

Cajeput Oil (*Oleum cajuputi*). Green; $d_{15°}$ 0,920[1]) to 0,930; very readily soluble in Spiritus.

[1]) It would be more correct to take 0,919 as the lower limit of value.

Carvone (*Carvonum*). Colourless or yellowish; $d_{15°}$ 0,960 to 0,964[1]); boiling point 229 to 230°; soluble in 2 parts spir. dil.

[1]) The specific gravity of pure carvone lies between 0,963 and 0,966.

Cinnamic Aldehyde (*Cinnamalum*). Obtained from cassia oil[1]); yellow; $d_{15°}$ 1,054 to 1,056[2]); soluble in every proportion in Spiritus; if 2 cc. cinnamic aldehyde are mixed with the same quantity sodium bisulphite solution (30%), and heated on a waterbath, a solid mass should be formed, which must dissolve completely when heated further and when 22 cc. bisulphite solution are gradually added; test for nitric acid; ferric chloride reaction.

[1]) The commercial cinnamic aldehyde is usually produced synthetically, as the production from cassia oil would be too expensive.

[2]) The specific gravity is also some times higher; we have observed in our own preparations up to 1,058.

Eugenol (*Eugenolum*). Colourless or yellowish, in course of time becoming brownish; $d_{15°}$ 1,072 to 1,074[1]); boiling point 252 to 254°[2]);

dissolves with difficulty in water, readily in Spiritus, ether, and glacial acetic acid. When 1 gm. eugenol is mixed with 26 cc. water and 4 cc. soda liquor (15%), a clear solution should be formed, which becomes cloudy on exposure to the air. Identity-reaction with ferric chloride and test for phenol.

[1]) The absolutely water-free preparation distilled *in vacuo*, is often also somewhat lighter; with our own distillates we have observed down to 1,0713. Comp. also Report April **1902**, 72.

[2]) It is difficult to determine the boiling point exactly as partial decomposition occurs in boiling.

Fennel Oil (*Oleum fœniculi*). Colourless or faintly yellow; $d_{15°}$ 0,965 to 0,975; soluble in an equal vol. Spiritus; when cooled down to a few degrees below 0°, fennel oil must separate off anethol crystals which melt again at + 5°[1]).

[1]) It would have been better to have substituted for the above, the requirement of a definite solidifying point which should not lie below + 4°. But it should be taken into consideration that the solidification may have to be started by inoculation with a small crystal of anethol, as under certain conditions it is possible to cool fennel oil strongly without causing solidification.

Oil of Juniper berries (*Oleum juniperi*). Colourless or greenish yellow; $d_{15°}$ 0,865 to 0,880[1]); dissolves with difficulty in Spiritus[2]).

[1]) The limits should here be wider: 0,860 to 0,885.

[2]) Only the freshly distilled oils dissolve in 5 to 10 vol. 90 per cent. alcohol; in the course of time the solubility diminishes very much.

Lavender Oil (*Oleum lavandulæ*). Colourless or faintly yellow; $d_{15°}$ 0,885 to 0,895; very readily soluble in Spiritus.

Lemon Oil (*Oleum citri*). Bright yellow; $d_{15°}$ 0,858 to 0,861; soluble in 5 parts Spiritus[1]).

[1]) Owing to its content of slimy and vegetable wax-like constituents, lemon oil forms mostly only a cloudy solution with 90 per cent. alcohol.

Mace Oil (*Oleum macidis*). Colourless or yellowish, becomes in course of time brownish; $d_{15°}$ 0,890 to 0,930; forms a clear solution with 3 parts Spiritus.

Menthol (*Mentholum*). Prismatic or needle-shaped colourless crystals; melting point 42 to 43°; dissolves with difficulty in water, readily in Spiritus, ether, and chloroform; 10 gr. menthol must be completely volatile at the temperature of the water-bath, without discolouring. If menthol is added to a mixture of 1 cc. glacial acetic acid, 3 drops concentrated sulphuric acid, and 1 drop nitric acid no coloration may occur.

Mustard Oil (*Oleum sinapis æthereum*). Colourless or yellow[1]); $d_{15°}$ 1,016 to 1,025; boiling point 148 to 152°; readily soluble in Spiritus and ether, little in water; the aqueous solution decomposes rapidly. Sulphuric acid reaction, and test with ferric chloride.

[1]) In the course of time mustard oil acquires a reddish brown colour.

Neroli Oil (*Oleum aurantii florum*). When freshly distilled colourless[1]) or faintly yellow, becoming darker in the course of time, and finally brown-yellow; $d_{15°}$ 0,870 to 0,880; dissolves very readily in spiritus; the spirituous solution shows a bluish fluorescence.

[1]) The fresh distillate also is never colourless, but always yellowish.

Peppermint Oil (*Oleum menthæ piperitæ*). Colourless, yellowish or greenish-yellow; $d_{15°}$ 0,900 to 0,910; forms a clear solution with 4 to 5 parts spir. dil. A mixture of 5 drops peppermint oil and 1 cc. glacial acetic acid must after a few hours show a blue coloration; the blue colour occurs more rapidly if to 2 cc. oil and 1 cc. glacial acetic acid, 1 drop nitric acid is added[1]).

[1]) Judging from the specific gravity, only English oil is admitted. For this reason it is all the more incomprehensible why the colour-reaction, which applies specially to American oil, has been included, which is of no importance whatever for judging the value of peppermint oil; even with the best Mitcham oil the reaction does not by any means occur in every case, a fact of which we have convinced ourselves repeatedly. In the presence of nitric acid a more or less powerful blue coloration occurs in every case.

Oil of Pinus pumilio (*Oleum pini pumilionis*). Colourless; $d_{15°}$ 0,865 to 0,875; commences to boil at 165°; completely soluble in Spiritus[1]).

[1]) For dissolving 1 vol. oil, 5 to 8 vol. 90 per cent. alcohol are required; sometimes a clear solution is not formed at all.

Rose Oil (*Oleum rosae*). Yellowish; $d_{20°}$ 0,855 to 0,870; solidifying point 15 to 22°; soluble in about 30 parts Spiritus with slight opalescence[1]).

[1]) Owing to its content of difficultly soluble paraffins, rose oil always forms only cloudy solutions with 90 per cent. alcohol, from which the paraffins gradually separate out.

Rosemary Oil (*Oleum rosmarini*). Colourless or yellowish; $d_{15°}$ 0,900 to 920; very readily soluble in Spiritus.

Sandalwood Oil, East Indian (*Oleum santali*). Bright yellow; $d_{15°}$ 0,975 to 0,980[1]); boiling point 275 to 305°; acid reaction; saponification number 5 to 15[2]); at 20 to 30° forms a clear solution with 5 parts spir. dil.

[1]) The upper limit is given too low and should be: 0,985.
[2]) The saponification numbers of sandal oil lie between 5 and 20.

Sweet Orange Oil (*Oleum aurantii pericarpii*). $d_{15°}$ 0,848 to 0,852; readily soluble in Spiritus[1]); in the course of time crystalline separations occur which are soluble in Spiritus[2]).

[1]) For dissolving 1 vol. oil, 8 to 10 vol. 90 per cent. alcohol are required, but the solution is never perfectly clear on account of the wax-like constituents always present in the oil.

[2]) The separations which are chiefly of the character of vegetable wax, dissolve with some difficulty in Spiritus.

Thymol (*Thymolum*). Colourless cristals in the form of tablets; melting point 50 to 51°; soluble in about 1100 parts water; readily soluble in Spiritus, ether, chloroform, and also in soda liquor; solid thymol sinks in water, but when melted it floats on the surface; when evaporated on a water bath, 10 gr. thymol must leave no weighable residue. Colour reactions.

Turpentine Oil (*Oleum terebinthinæ*). Colourless or faintly yellow; $d_{15°}$ 0,865 to 0,870[1]); commences to boil at 160°; forms a clear solution with about 8 parts Spiritus; it absorbs oxygen from the air, and then becomes more viscid.

[1]) The crude oil is frequently heavier, up to 0,877.
[2]) Turpentine oil commences to boil at about 155°.

Turpentine Oil, rectified (*Oleum terebinthinæ rectificatum*). Colourless; $d_{15°}$ 0,860 to 0,870; boiling point 155 to 162°; soluble in about 7 parts Spiritus; the solution should not change litmus paper moistened with water.

Valerian Oil (*Oleum valerianæ*). Yellow-green or brown-yellow; at first mobile, becoming more viscid in course of time; $d_{15°}$ 0,93 to 0,96; acid reaction; dissolves with difficulty in water, very readily in Spiritus.

Spanish Pharmacopœia.

(Farmacopea oficial española, séptima edición 1905.)

On the new seventh edition of the Spanish Pharmacopœia, it is unfortunately not possible, so far as concerns the articles which interest us, to pronounce as favourable an opinion as on the other Pharmacopœias discussed in these pages. At first sight it no doubt appears as if a modern spirit pervaded throughout the directions for testing, as the Pharmacopœia even specifies definite demands for the optical rotatory power of the oils; but on closer examination the exact opposite is found to be the case. For example, the rotations given are partly entirely incorrect, and many of the other details are so antiquated that one involuntarily receives the impression that the knowledge of the progress made in the examination of essential oils during the last 20 years, has not yet penetrated to Spain. This fact makes it appear all the more desirable to discuss here the individual oils.

In vain we have looked for information as to the temperature to which the specific gravities mentioned for the various oils apply.

As for other liquids they have all been taken at 15°, it may be assumed that in the case of essential oils that temperature has also been taken as a basis. For this reason we have in the following pages judged the specific gravities in every case accordingly.

Of alcohols, there are admitted an alcohol of 95° (95 per cent. by volume), and one of 60° (60 per cent. by volume).

Anise Oil (*Esencia de anís*). Colourless; $d_{15°}$ 0,984 to 0,986[1]); solidifies at + 10° into a white crystalline mass[2]); soluble in alcohol in every proportion; the alcoholic solution must not redden litmus paper, and its colour must not change when ferric chloride is added.

[1]) As solidification sometimes occurs already spontaneously at 15°, it is advisable to determine the specific gravity at 20°; the limits of value lie between 0,980 and 0,990, those given above are incorrect.

[2]) Solidification has frequently to be started by inoculation with a small crystal of solid anethol, as anise oil can under certain conditions be cooled very much without solidifying. The solidification point of good oils lies above + 17°; for the determination, comp. Gildemeister and Hoffmann, "The Volatile Oils", p. 187.

Bergamot Oil (*Esencia de bergamota*). Obtained from the peel of the bergamot by expression or by distillation with water vapour[1]); yellowish-green or green[2]); $d_{15°}$ 0,86 to 0,88[3]); α_D to the right; soluble in one half volume 85 per cent. alcohol, and in potash liquor[4]); 4 vol. oil form a clear solution with 1 vol. carbon disulphide, which becomes cloudy when more carbon disulphide is added.

[1]) The oil obtained in the usual manner by distillation with water vapour is inferior. Comp. Gildemeister and Hoffmann, "The Volatile Oils", p. 474.

[2]) Bergamot oil has also frequently, especially in the fresh state, a brown or honey colour. Distilled bergamot oil is colourless.

[3]) The specific gravity of the oil obtained by expression lies between 0,881 and 0,886; the distilled oils are somewhat lighter (0,865 to 0,880).

[4]) In ordinary aqueous potash liquor bergamot oil is not soluble.

Bitter Almond Oil (*Esencia de almendras amargas*). When freshly distilled, colourless, subsequently yellowish; $d_{15°}$ 1,043[1]); $\alpha_D \pm 0°$[2]); soluble in 30 parts water[3]), in every proportion in alcohol and ether. It should not react[4]) violently with iodine which dissolves slowly in it; when mixed with sulphuric acid it should acquire a brown colour which disappears again almost completely when alcohol is added. If a mixture of 1 part oil, 8 parts alcohol and 1 part potash is heated until 2/3 of the alcohol have evaporated, no crystalline residue should remain behind, and the liquid should have a yellowish-brown colour.

[1]) The specific gravity lies at 15° between 1,045 and 1,070.

[2]) Sometimes a very slight optical activity is observed.

[3]) The solution is not complete even if more water is added; the bulk of the oil separates out again when the mixture is left standing.

[4]) Such reactions are of no importance whatever for judging essential oils; for this reason they are not mentioned again in the following pages. The same applies to tests of a similar character, as for example colour-reactions.

Cajeput Oil (*Esencia de cayeput*). Colourless, yellowish-green, or emerald green; $d_{15°}$ 0,91 to 0,95[1]); $\alpha_D \pm 0°$[2]); neutral; readily soluble in alcohol and acetic acid and alcohol, but not in carbon disulphide[3]).

[1]) The limits of value might have been drawn narrower; $d_{15°}$ 0,919 to 0,930.

[2]) Cajeput oil is slightly lævorotatory, α_D to — 2° 40′.

[3]) All essential oils dissolve in carbon disulphide; any cloudiness occurring thereby must be attributed to the small content of water due to the manner of production of the oils.

Cinnamon Oil, Ceylon (*Esencia de canela*). Golden yellow, in course of time reddish; $d_{15°}$ 1,004 to 1,006[1]); α_D slightly to the left; nitric acid test, ferric chloride reaction.

[1]) Ceylon cinnamon oil has at 15° a specific gravity of 1,023 to 1,040.

Citron Oil[1]) (*Esencia de cidra*). Obtained from the peel of the cedro or citron by expression or distillation with water vapour[2]); colourless[3]) or yellowish; $d_{15°}$ 0,852 to 0,856[4]); α_D to the right; soluble in every proportion in carbon disulphide and in 95 per cent. alcohol; with weaker alcohol cloudy solutions are formed[5]).

[1]) As citron oil is not a commercial article, its admission to the Pharmacopœia is difficult to explain.

[2]) The oils obtained by distillation are inferior.

[3]) Only the distilled oils are colourless.

[4]) With reference to the specific gravity of citron oils, comp. our Reports April **1902**, 30, October **1902**, 35, and April **1903**, 34.

[5]) The solutions in carbon disulphide are usually slightly turbid owing to the content of water in the oil; of 95 per cent. alcohol about 0,5 to 1 vol. are required to form a clear solution.

Clove Oil (*Esencia de clavo*). Freshly distilled colourless, subsequently yellowish, reddish, or brown; $d_{15°}$ 1,04 to 1,06[1]); α_D to the left; acid reaction; ferric chloride must not cause blue coloration.

[1]) The specific gravity is occasionally also higher, up to 1,07 (15°).

Eucalyptol (*Eucaliptol*). Colourless; $d_{0°}$ 0,940[1]); at a low temperature solidifying into a crystalline mass, which melts again at 1°[2]); boils at 174°[3]); soluble in every proportion in absolute alcohol, in carbon disulphide and in glacial acetic acid.

[1]) The specific gravity of eucalyptol at 15° is 0,928 to 0,930.

[2]) The melting point does not lie at +1°, but at —1°.

[3]) Eucalyptol boils at 760 mm between 176 and 177°.

Eucalyptus Oil (*Esencia de eucalipto*). Colourless or yellowish; $d_{15°}$ 0,90 to 0,92[1]); α_D to the right; neutral; soluble in an equal part by weight of alcohol.

[1]) More correct is an upper limit of 0,93.

Lavender Oil (*Esencia de espliego*). Colourless, yellowish or greenish-yellow; $d_{15°}$ 0,87 to 0,94[1]); α_D to the left; acid reaction; soluble in every proportion in 85 per cent. alcohol.

The oil of *Lavandula spica* D. C. is dextrorotatory.

[1]) The limits of value are here so far apart, that most adulterated oils would also answer the requirements; with pure oil, the specific gravity fluctuates between 0,882 and 0,895 (15°).

Lemon Oil (*Esencia de limón*). Obtained from the peel of the lemon by expression or distillation by water vapour[1]). The oil obtained

by expression is yellowish and turbid[2]), separating off stearoptene[3]) at — 20°, possessing a very pleasant odour; the distilled oil is colourless and has a less pleasant odour; $d_{15°}$ below 1; α_D to the right[4]); soluble in ether and 95 per cent. alcohol, forms only cloudy solutions with 85 per cent. alcohol.

[1]) Distillation of the oil is quite irrational, as such oils rapidly deteriorate and then acquire an unpleasant pungent odour.

[2]) At ordinary temperature lemon oil is mostly clear; a possible turbidity is caused by slimy or vegetable wax-like constituents.

[3]) The separation called "stearoptene" consists of substances of the character of vegetable wax.

[4]) More precise *data* would here be very much to the point. The specific gravity of good lemon oil obtained by expression lies between 0,857 and 0,861 (15°) and the rotation between + 58 and + 65° (at 20° C).

[5]) Of 95 per cent. alcohol about 1 vol. is required to form a solution.

Menthol (*Mentol*). Colourless needles; $d_{15°}$ 0,89; α_D to the left; melting point 42°[1]); boiling point 208°[2]); scarcely soluble in water, readily soluble in alcohol, ether, chloroform, and fatty oils; volatilises without residue.

[1]) Melting point 42 to 43°.

[2]) Boiling point 212° (760 mm).

Mustard Oil (*Esencia de mostaza negra*). Colourless or yellowish; when exposed to the air, decomposition occurs with red or brown coloration; $d_{15°}$ 1,018[1]); boiling point about 148°[2]); readily soluble in alcohol, ether, and chloroform; should not contain any fatty oil; a solution of 1 part mustard oil in 5 parts alcohol must not be coloured red or blue by ferric chloride.

[1]) The specific gravity of mustard oil at 15° fluctuates between 1,014 and 1,025.

[2]) On distillation the bulk of mustard oil passes over between 148 and 153°.

Neroli Oil (*Esencia de azahar*). Colourless[1]), in course of time yellowish; $d_{15°}$ 0,85 to 0,90[2]); α_D to the right; neutral[3]); when at rest, separation of a white crystalline mass, which dissolves with difficulty in alcohol. Taste aromatic, not bitter[4]).

[1]) Neroli oil is never colourless, but right from the first yellowish; in course of time it becomes reddish-brown.

[2]) The specific gravity lies between 0,870 and 0,880.

[3]) Oils containing ester show almost always a minute content of free acid.

[4]) The after-taste is somewhat bitter.

Peppermint Oil (*Esencia de menta piperita*). Colourless or yellowish green; $d_{15°}$ 0,89 to 0,92; α_D to the left; acid reaction; readily soluble in alcohol.

Rosemary Oil (*Esencia de romero*). Colourless or yellowish; $d_{15°}$ 0,88 to 0,91[1]); α_D to the left[2]); neutral reaction; soluble in every proportion in 85 per cent. alcohol[3]).

[1]) More correct would be 0,89 to 0,92.

[2]) Pure rosemary oil is dextrorotatory; lævorotation would point to adulteration with French oil of turpentine.

[3]) Rosemary oil is also frequently not soluble in every proportion in 85 per cent. alcohol.

Sandalwood Oil, East Indian (*Esencia de sándalo*). Bright yellow; $d_{15°}$ 0,970 to 0,985; α_D to the left; neutral or weak acid reaction; readily soluble in alcohol.

Sassafras Oil (*Esencia de sasafrás*). Freshly distilled colourless or bright-yellow; subsequently yellow to reddish; $d_{15°}$ above 1; α_D to the right; neutral reaction; soluble in 4 to 5 parts 85 per cent. alcohol.

Sweet orange Oil (*Esencia de naranja*). Obtained from the peel of the fruit of *Citrus aurantium* Risso by expression or distillation by water vapour[1]); colourless or bright yellow[2]); $d_{15°}$, according to the method of production, 0,835 to 0,844[3]); α_D + 82°[4]); readily soluble in absolute alcohol, ether, and fatty oils.

[1]) It is not expedient to produce the oils by ordinary distillation with water vapour, as distilled oils readily deteriorate and then acquire a stale, unpleasant odour.

[2]) Only the distilled oils are colourless, the colour of expressed oil is yellow to yellow-brown.

[3]) The specific gravity of sweet orange oil lies at 15° between 0,849 and 0,853; distilled oils are somewhat lighter.

[4]) Commercial oil at 20° rotates between + 95° 30′ and + 98°; to what kind of oil the rotation mentioned above applies is incomprehensible.

Terpin hydrate (*Terpina*)[1]). Colourless and odourless prisms which melt at 116° with loss of water; soluble in 250 parts cold and 32 parts boiling water, readily soluble in alcohol and ether, further in glycerin and in oil of turpentine; when boiled with greatly diluted sulphuric acid, terpineol is formed; it must not have a turpentine odour, and its aqueous solution must not redden litmus paper; burns with a highly luminous flame without leaving any residue.

[1]) The Pharmacopceia mentions *terpina*, but means terpin hydrate. As terpin and terpin hydrate are two different compounds, a more exact description would have been necessary.

Terpinol[1]) Colourless or faint yellow; $d_{15°}$ 0,852; α_D ± 0°; boiling point 168°; dissolves with great difficulty in water; soluble in alcohol and ether. By the action of nitric acid it is converted into terpin hydrate.

[1]) A compound terpinol does not exist. What used to be called terpinol is, according to Wallach's researches, a mixture of terpineol and terpenes. Comp. Liebig's Annalen **230** (1885), 271.

Thyme Oil (*Esencia de tomillo*). Colourless or yellowish[1]); $d_{15°}$ 0,89[2]); α_D to the left; neutral reaction; soluble in an equal volume 85 per cent. alcohol.

[1]) Thyme oil is usually somewhat dark in colour, and the rectified oils frequently acquire again in a short time the red-brown colour of the crude oil.

[2]) This value must be considered as the lowest limit of the specific gravity.

Thymol (*Timol*). Large crystals of the melting point 44°[1]) and boiling point 230°. Very little soluble in water (about 1:340), readily soluble in alcohol, ether, and glacial acetic acid, in fatty oils and the alkalies. The aqueous solution must be neutral, and not become discolored when ferric chloride is added; when heated on a water bath, thymol should leave no residue.

[1]) Thymol melts at 50 to 51°.

Turpentine Oil (*Esencia de trementina*). Colourless; $d_{15°}$ 0,85 to 0,87[1]); α_D, according to origin, to the left or right; soluble in ether, chloroform and absolute alcohol in every proportion, also in 4 vol. 90 per cent. alcohol, and in 12 vol. 81 per cent. alcohol[2]).

[1]) The specific gravity is also frequently higher, up to 0,877.

[2]) Turpentine oil dissolves in 5 to 7 vol. 90 per cent. alcohol, and in 12 to 14 vol. 81 per cent. alcohol.

Chemical Preparations and Drugs.

Benzaldehyde. We have convinced ourselves that the products described in commerce as "free from chlorine" do not always deserve this designation; we would recommend purchasers to pay special attention to this point, and send us samples for testing. The removal of the last traces of chlorine is not such a simple matter, but is necessary if the product is to be described as absolutely free from chlorine.

Benzyl acetate. This preparation, which within the last few years has come greatly in favour on account of its pleasant fruity odour, is also supplied by us absolutely free from chlorine, and, as we manufacture it on a large scale, we can offer it at a very advantageous price.

Benzyl benzoate, a constituent of Peru balsam, is also well introduced, and is used chiefly as a fixing agent for highly volatile perfumes; it is specially adapted for this purpose on account of its balsamic odour and great stability. It is also recommended as a solvent for artificial musk.

Citral. Improved manufacturing processes and a production on a constantly growing scale enable us to meet all competition in this article. The use of it is growing more and more, since the prejudices have been overcome with which this body was received when we discovered it some 18 years ago, and introduced it to the consumers.

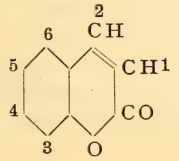
Coumarin. A work by Ph. Chuit[1]) and Fr. Bœlsing supplies a valuable contribution towards the knowledge of the coumarins alkylised in the benzene nucleus, of which up to the present little was known. In order to arrive at 3-methyl coumarin[2]), they condensed, according to Knœvenagels[3]) method, malonic acid with o-homosalicylic aldehyde, with application of aniline hydrochloride. The resulting product of condensation, 3-methyl coumarin carboxylic acid, forms white needles of the melting point 142 to 143°. On distillation at ordinary pressure it yields 3-methyl coumarin of the boiling point 178° (20 mm. press.); melting point 109 to 110°. This body has a faint odour of coumarin. 3-Methyl 1-aceto coumarin forms odourless, faintly yellow crystals of the melting point 125,8 to 126,2°.

Its phenyl hydrazone melts at 168 to 169°, its semicarbazone at 224 to 225°. 3-Methyl coumarin carboxylic acid ester is formed during the condensation of the above aldehyde with malonic acid ester, with application of piperidine as condensing agent; odourless, brilliant crystals of the melting point 81°.

The above-mentioned chemists proceeded in an entirely analogous manner to produce the remaining homocoumarins and their derivatives. Contrary to H. Schmidt[4]), who obtained by Perkin's method from m-homosalicylic aldehyde, by heating with acetic acid anhydride and sodium acetate to 220°, a methyl coumarin melting at 90°, Chuit and Bœlsing arrived at two different methylated coumarins. They proved at the same time that Schmidt's preparation was a mixture of two homocoumarins, whose formation could be thus explained, that the m-homosalicylic aldehyde used for the condensation was a mixture of two isomerides, methyl phenol-3-methylal-4 and methyl phenol-3-methylal-2. The first aldehyde of the melting point 59° yields on condensation with malonic acid, 4-methyl coumarin-1-carboxylic acid of the melting point 198,8 to 199,8°. The 4-methyl coumarin which can be obtained from it, melts at 125,8° to 126,4°, and has a fairly strong odour of coumarin. The other m-homosalicylic aldehyde, methyl phenol-3-methylal-2, of the melting point 31,5°, condenses

[1]) Bull. Soc. Chim. III. **35** (1906), 76.

[2]) The coumarin formula is based on the designation of Simonis and Wenzel (Berl. Berichte **33** [1905], 2327): —



[3]) Berl. Berichte **31** (1898), 2585, 2696.

[4]) Thesis, Rostock 1897.

with malonic acid to 6-methyl coumarin-1-carboxylic acid of the melting point 162,5 to 163°. The 6-methyl coumarin corresponding to it has the melting point 65 to 65,8°. It possesses only a feeble coumarin odour. The two methyl coumarins produced by the authors according to Perkin's method, show the same melting point, which disproves Schmidt's observation. The 4-methyl coumarin-1-carboxylic acid ester which can be derived from the methyl phenol-3-methylal-4, and which is obtained in a manner analogous to the method described above, forms brilliant leaflets, which melt between 101,5 and 102,5°. 4-methyl-1-aceto coumarin of the melting point 156 to 157° yields an oxime which melts at 224°. The other carboxylic acid ester which is derived from methyl phenol-3-methylal-2, forms brilliant needles of the melting point 122 to 122,5°. 6-methyl-1-aceto coumarin shows the melting point 115°, its oxime that of 214°.

The condensation of p-homosalicylic aldehyde (methyl phenol-4-methylal-3) with malonic acid leads to 5-methyl coumarin carboxylic acid of the melting point 166,8°. Its ester forms odourless, transparent tablets of the melting point 103 to 104°. 5-methyl coumarin has, of all the homocoumarins described, the most powerful odour, but it differs slightly in the odour from ordinary coumarin. The latter is more penetrating, but not so persistent as the former. In view of the high price of p-homosalicylic aldehyde, or p-cresol, 5-methyl coumarin appears hardly capable of competing with ordinary coumarin. 5-methyl coumarin boils at 14 mm. pressure at 174°, and melts at 74,6 to 75°. Its acetyl derivative of the melting point 128 to 128,4°, is obtained in a manner analogous to the former; semicarbazone melting point 211°; oxime melting point 219°; phenyl hydrazone melting point 193 to 194°.

The same authors[1]) have subsequently published the results of their examination of the two above-mentioned m-homosalicylic aldehydes. A separation of these bodies, produced, according to the method of Tiemann and Schotten[2]), by the action of chloroform on m-cresol, can be effected by repeated treatment of the aldehyde mixture with small quantities of dilute soda liquor, when only the aldehyde of the melting point 59° is dissolved. Another method of separation is based on the different solubilities of their calcium salts in hot water. The calcium salt of methyl phenol-3-methylal-2 of the melting point 32° dissolves with difficulty, and is precipitated in the form of yellowish crystals, when a hot dilute solution of calcium chloride is added to the hot soda liquor solution of the aldehyde mixture, whilst the salt of the methyl phenol-3-methylal-4 melting at 59° remains in solution in the mother-liquor and only separates out on cooling.

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[1]) Bull. Soc. Chim. III. **35** (1906), 129.
[2]) Berl. Berichte **11** (1878), 773.

The methyl phenol-3-methylal-4 purified from the calcium salt, melts at 59 to 59,8°, and boils at 219 to 221° (726 mm. pressure). It has a very pleasant odour, reminding of that of pure salicylic aldehyde. Melting point of the oxime 108,5 to 109°; melting point of the semicarbazone 254 or 272°; melting point of the phenyl hydrazone 160 to 160,5°. When heated with caustic potash to 220°, it oxidises into m-cresotinic acid (α-m-homosalicylic acid) of the melting point 176°; its methyl derivative yields with the same reaction also m-cresotinic acid, and on oxidation with potassium permanganate methoxyterephthalic acid of the melting point 277 to 279°. From these results the constitution of the aldehyde is at once apparent. Its isomeride, methylphenol-3-methylal-2 of the melting point 31,4 to 31,9° boils at 728 mm. pressure at 228 to 229,3°. The odour of this body resembles that of salicylic aldehyde. Melting point of the oxime 111 to 112°; melting point of the semicarbazone 214 or 244° respectively; melting point of the phenyl hydrazone 170,2 to 171,4°. Caustic potash converts it a 220° into β-m-homosalicylic acid of the melting point 168 to 169°. Its methyl ether is converted on oxidation with potassium permanganate into 3-methoxy-o-toluylic acid of the melting point 139°.

Eucalyptol (cineol), crystallising. We would here again call attention to the fact that we only manufacture the pure body. This has a melting point of — 1°, and is optically inactive. We lay special stress on these properties, as they are characteristic of the pure body, and as products are met with in commerce which are offered as eucalyptol, but which are nothing else than a rectified eucalyptus oil. Such makeshifts can naturally be supplied at a decidedly lower price than our product.

Geraniol from palmarosa oil. With the low price of palmarosa oil, this preparation now comes cheaper than the one prepared from citronella oil, and can be supplied in any quantity. It possesses a fine rose-like odour, and deserves to be submitted to a thorough test.

Heliotropin. The price of this product has now reached the extreme limit of possibility. In consequence of this the use has increased tenfold during the last few years.

Linalyl acetate. This body, as is well known, is the characteristic principal constituent of lavender oil and bergamot oil. It is manufactured by us by chemical process in the pure state, and contains about 80% linalyl acetate; the remainder of about 20% consists of linalool, which is also present in the free state in oil of bergamot.

Linalyl acetate is therefore to be considered as a concentrated terpeneless bergamot oil, practically about 2 1/2 times stronger than

ordinary oil of a good quality. Although the price does not at present permit the use on a large scale, it is possible that under favourable circumstances linalyl acetate might come to play the part of a substitute of bergamot oil. If only from this point of view, the manufacture of linalyl acetate must be welcomed.

In the perfumery trade it can be used in every case where the bulk of ordinary bergamot oil in the manufactured product is inconvenient.

A further advantage is its being absolutely colourless.

Menthol. With regard to the commercial situation of this preparation, the same applies as what has been said on p. 53 of the present Report on the subject of Japanese oil of peppermint. Here also the bears and bulls are standing face to face, and it is doubtful which of the two will finally carry the day. The result will to a large extent depend upon this, whether the cultivation of peppermint in Japan has actually been restricted as stated, or whether that statement has only the character of a hollow phrase.

It is a fact that the consumption of menthol is still going up, and that the number of medicinal and cosmetic preparations based on menthol is constantly increasing. In view of the probably unique usefulness and popularity of menthol, a decline of the value is in our opinion scarcely to be expected; on the contrary, the present prices should be taken advantage of for laying in an abundant stock for the current year.

This suggestion is fully supported by the statistical figures, for only in the years 1888 and 1889 has the price of purified menthol been lower than now. This article made its first appearance in our lists in March 1881, at 140 marks per kilo, then kept itself for a long time at 100 marks, and subsequently took a pronounced downward course, with periodical upward movements.

Total value of menthol shipments from Japan in the years 1900 to 1904.

	1900	1901	1902	1903	1904
	Yen	Yen	Yen	Yen	Yen
to British India . .	20875	18807	11698	23020	63955
„ France	4950	25212	22565	43317	141075
„ Germany . . .	46391	100040	71045	193729	159496
„ the United Kingdom	62995	9706	90833	155406	229685
„ Hong Kong . .	13964	163884	127369	219189	156775
„ the United States .	23000	111130	126525	162754	326784
„ other countries . .	326	8273	13684	6987	12973
Totals	172501	437052	463719	804402	1090743

Safrol. The advancing prices of camphor oil will in course of time have to be taken into consideration in calculating the price of safrol. For the present we are still working up material bought by us at low prices and for that reason have still refrained from raising our quotations.

Terpineol. On the basis of the present prices of oil of turpentine, the quotations of terpineol ought to be raised considerably but for the fact that these unfavourable conditions are counteracted by improvements in the manufacture.

We produce only one quality, which is of the greatest purity and possesses an incomparable fragrance. In spite of the large increase in our plant, we are scarcely able to meet the demand — the best proof, no doubt, of the excellent quality of our product.

We have in our Reports repeatedly warned against attaching too great a value to colour reactions in the terpene chemistry. In spite of this, new ones are recommended again and again, which often already at the outset appear of little value. This, for example, is the case with the reaction mentioned by C. Reichard[1]) for the detection of terpineol in mixtures of perfumes, essential oils, etc. This reaction is accomplished as follows: — In a small porcelain dish are given a few drops of a strong aqueous solution of potassium thiocyanate; this is heated until a slight crust of solid salt separates out at the margin of the liquid, and a small drop of terpineol is then added. If a drop of concentrated sulphuric acid is added to this mixture starting from the edge, there occurs at ordinary temperature immediately an intense coloration which usually appears to be brown-red, but, according to the degree of concentration of the solution of potassium thiocyanate, the shades of colour observed may be blood-red, purple, or brown. Turpentine oil and terpin hydrate also give this reaction. If instead of potassium thiocyanate, a solution of sodium bisulphite is used, but for the rest the reaction is accomplished in the same manner, a beautiful blood-red mixture is obtained.

As other terpene compounds react the same as terpineol, a practical utilisation of this reaction is out of the question.

Thiosinamine, the excellent effect of which in cicatrisation after burns, etc., was already mentioned in our last Report[2]), has lately also been warmly recommended by Mellin[3]). It is used in

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[1]) Pharm. Centralhalle **46** (1905), 971.
[2]) Report October **1905**, 127.
[3]) Accord. to Therap. Monatsh. **12** (1905), 650.

practice in the form of an injection in a 15 to 20 per cent. solution. Injections of 10 per cent. aqueous solution with glycerin are, however, less painful.

Thymol. It has no doubt been a surprise to everyone interested in the manufacture of this article, that, according to the new German Customs Tariff, the crude material, i. e. the ajowan-seed which is quite unsuitable for consumption, and which was formerly free of duty, has now been taxed with an import duty of 4 marks per 100 kilos, and has therefore been included among the so-called spice-seeds, such as anise, fennel, caraway, etc. Why this has been done, is inexplicable to the expert, because, as ajowan-seed is exclusively worked up for thymol, and for this purpose is admitted free, and is moreover a tropical product which cannot be grown in Germany, the duty on it will not bring in a single penny, and it would have been better if it had been left duty-free.

The prices of ajowan-seed in India remain firm at about 11/- per cwt.; our heavy old stock was still bought at 8/-, so that we were able to avoid the high quotations of last year.

According to Schill[1]), thymol is a good remedy against gnats. It is used in the form of a solution of thymol in 50 per cent. alcohol (2 : 100) which is rubbed on the hands, neck, and face by means of a cotton wool pad or a piece of woollen rag. This keeps the gnats away. Against stings it is recommended to make a paste of bicarbonate of soda and water and apply it to the sting, or to carry it about in a saturated solution and dab it repeatedly on the sting. It is, no doubt, a matter of general knowledge that bicarbonate of soda applied in the same manner, also gives excellent results in slight burns.

Vanillin. Jos. Hanuš[2]) reports on the quantitative estimation of vanillin in vanilla extracts. He employs as a suitable reagent for the estimation of vanillin in vanilla, vanilla goods, and vanilla extracts, m-nitrobenzhydrazide, by means of which, in aqueous solution, all the vanillin is precipitated quantitatively. This method is recommended particularly for this reason, that its exactness does not suffer even from the presence of the ordinary adulterants, such as acetanilide, benzoic acid, sugars, or salicylic acid. It is, however, useless if other aldehydes are present, especially piperonal, whose presence in vanillin can be detected by bromine water, with which piperonal rapidly forms needles with a silken lustre.

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[1]) Schweiz. Wochenschr. f. Chem. u. Pharm. **1905**, No. 24, accord. to Pharm. Centralh. **47** (1906), 157.

[2]) Zeitschr. Untersuch. der Nahrungs- und Genußmittel **10** (1905), 585 to 591. Accord. to Chem. Centralbl. **1906**, I. 89.

For the purpose of the determination, liquids are employed which contain 0,05 to 0,15 gm. vanillin. A solution which contains in 10 cc. hot water $1^1/_2$ times the theoretically required quantity of m-nitrobenzhydrazide, i. e. 0,1 to 0,25 gm., is added to the vanillin solution; this is left standing in a stoppered vessel with occasional shaking for 24 hours, then filtered through a Gooch's crucible, washed with cold water, dried for 2 hours at 100 to 105°, and then weighed. By multiplying the quantity (in grams) of the weighed condensation-product of the formula

$$NO_2 \cdot C_6H_4 \cdot NH \cdot N : CH \cdot C_6H_3 \cdot (OCH_3) \cdot (OH)$$

with 0,4829, the quantity of vanillin is obtained. In order to determine the vanillin-content in the vanilla pods, about 3 gm. are extracted for, say, 3 hours with ether (at most 50 cc.), the solvent then evaporated at 60°, next dissolved in 50 cc. water, and, as indicated above, the condensation product of vanillin precipitated with m-nitrobenzhydrazide. As the ethereal extract of vanilla pods contains fat, the reaction mass, in order to remove the fat, is three times extracted with petroleum ether. The petroleum ether solution is passed through the Gooch's crucible, and only then is the vanillin-m-nitrobenzhydrazone placed in the crucible, and washed with petroleum ether previous to drying. In the case of alcoholic vanilla extracts, the alcohol must first be carefully evaporated.

Contrary to Preusse's[1]) observations, Y. Kotake[2]) found in the urine of rabbits to which vanillin had been administered, the presence of a lævorotatory substance. In the animal body vanillin experiences an oxidation into vanillinic acid which is partly separated off in the urine in the form of glycurovanillinic acid. Basic lead acetate precipitates it from its solution. It is lævorotatory, and does not reduce alkaline copper solution. By boiling with dilute sulphuric acid it is split up into vanillinic acid and glycuronic acid.

Musk. A report of Mr. Alexander Hosie[3]), Consul General at Chengtu, gives some interesting information on the musk-trade. A journey which he undertook in July 1904 on the Eastern borders of Thibet brought him to Tachienlu, the capital of the province Szuchuan, of which one of the most valuable commercial products is musk, which is bartered chiefly for tea, silk, atlas and cloth. At Tachienlu, the

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[1]) Zeitschr. f. physiol. Chem. **4** (1877), 213.

[2]) Zeitschr. f. physiol. Chem. **45** (1905), 320. Accord. to Chem. Ztg. Repert. **29** (1905) 328, and Chem. Centralbl. **1905**, II. 690.

[3]) A Journey to Thibet. Chemist and Druggist **67** (1905), 651.

real centre of the trade, the Chinese ounce fetches 10 taels (1 tael = about 2/8). At Chengtu the price is already raised to 18 to 19 taels, but for pure musk as much as 29 to 30 taels are asked. At Szuchuan the musk is already subject to frequent adulterations. In order to detect these, certain definite methods are employed there. If the odour is not satisfactory, or if other doubts exist as to the genuine character, a small incision is made in the musk-bag, a sample taken out, and thrown in water. If the sample remains crumbly, the musk is genuine, but if it dissolves, it is adulterated. Or a sample is placed on a glowing piece of charcoal; if it melts and swells up, the musk is good; if it suddenly becomes hard, it must be regarded as adulterated. The annual sale of musk-bags at Tachienlu for Chinese and foreign markets, is estimated at 1100 to 1200 catties (24533 Chinese ounces, value £ 48750).

In spite of the great importance of musk in commerce, very little is known of its chemical composition. Total darkness exists especially with regard to the character of the odoriferous substances which alone determine the value of this product. For this reason we considered it opportune to take in hand the solution of this question which is of so much importance both from a scientific and a technical point of view[1]). In the first place, we determined, by distilling out 500 gm. musk with water-vapour for many days the content of odoriferous substances volatilisable with water-vapour in the natural product. The distillation-water hereby obtained, on which but a small quantity of oil floated, yielded by means of careful extraction with ether a total of 7 gm. of a dark-brown oil with a very unpleasant odour, equal to 1,4% of crude musk oil. The examination of this oil showed that it consists partly of a ketone, which forms a well-crystallizing semicarbazone. From the latter the ketone could again be separated off, by boiling with dilute sulphuric acid, in the form of an oil with a strong musk-like odour. In order to obtain a better knowledge of the properties of the new ketone, large quantities of musk had to be worked up. But it was found convenient to extract the musk first with ether, and then to distil out, with water-vapour, the extract obtained. It was then found that the content of musk oil in various specimens of musk, which to all appearances were of equally good quality, may differ considerably.

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[1]) German Patent application by Schimmel & Co. No. 23255, IV. Cl. 23a, of 26th Jan. 1905. A notice on muskone, abstracted by H. Mann from our circular, is published in the Seifensiederzeitung **33** (1906), 54; rep. Chem. Zeitg. Repert. **30** (1906), 51. Muskone is introduced in commerce as "muskone solution" dissolved in 50 per cent. alcohol, and not (as stated in the report) dissolved in alcohol in the proportion of 50%.

For example from 1 kilo musk, 5 gm. = 0,5% crude musk oil were obtained, and from 3 kilos 21,2 gm. = 0,7%, whilst another consignment yielded 62 gm. = 2,07% oil from 3,051 kilos.

Muskone. The crude musk oil, as obtained by extracting the distillation-water with ether, still contains free fatty acids, and saponifiable constituents (fats). For this reason it was heated, for further purification, for a short time with a small quantity of alcoholic potash, and after separating off and washing with water, fractionated *in vacuo*.

After this treatment 62 gm. crude oil distilled as follows: —

I. fraction: 65 to 160° at 7 mm. 12,5 gm.
II. fraction: 160 to 166° at 7 mm. 36,3 gm.

There remained back a fairly considerable, brown residue. After fractionating once more we obtained 37,5 gm. (1,2% of the musk) of a fraction boiling at 145 to 147° at 3 mm pressure, which consisted almost exclusively of the new ketone, for when treated with sodium acetate and semicarbazide hydrochloride, it solidified completely into the solid semicarbazone.

When this principial fraction was once more submitted to distillation, 30 gm. distilled from 142 to 143° at 2 mm. pressure. The remainder passed over up to 145°.

The constants of the ketone were as follows: boiling point 142 to 143° (2 mm. pressure), 327 to 330° (752 mm. pressure), $d_{15°}$ 0,9268, α_D — 10° 6′ $n_{D25°}$ 1,47900.

This ketone, to which we have given the name "muskone" is the sole bearer of the natural musk-odour. As it has been freed from all disagreeable secondary odours of the musk-secretion, it reproduces the musk-aroma in a hitherto unknown strength and fineness. Muskone is a colourless viscid oil, which is miscible with alcohol in every proportion.

The analysis of muskone gave the following values: —

I. 0,1202 gm. of the substance: 0,3544 gm CO_2, 0,1356 gm. H_2O.
II. 0,1593 gm. of the substance: 0,4706 gm. CO_2, 0,1818 gm. H_2O.

	Found: I	II	Calculated for $C_{16}H_{30}O$	$C_{15}H_{28}O$
C	80,41%	80,57%	80,57%	80,25%
H	12,54%	12,68%	12,70%	12,60%

Nitrogen and sulphur could not be detected in the ketone.

With hydroxylamine and semicarbazide, muskone forms crystallising compounds. The semicarbazone is specially characteristic, and suitable for the detection. The latter is obtained by mixing 1 gm. muskone with 1 gm. sodium acetate and 1 gm. semicarbazide hydrochloride with a little alcohol into a paste, and letting it stand for some time. When

water is added, the semicarbazone is precipitated as a white, solid mass, which melts after repeated recrystallisation from alcohol at 133 to 134°. The muskone semicarbazone crystallises in fine, white prisms, which are absolutely odourless. If a trace of it is heated with dilute sulphuric acid, a powerful pure musk-odour soon proclaims that muskone has been split off. The analysis of the semicarbazone gave values on combustion, from which either the formula $C_{16}H_{31}ON_3$ or $C_{17}H_{33}ON_3$ can be calculated. Muskone has consequently either the composition $C_{15}H_{28}O$, or $C_{16}H_{30}O$.

We are at this moment still occupied with the further examination of muskone, and hope to report on this at a later date.

The question whether the natural odoriferous substance of musk is identical with the so-called "artificial musk Baur" (trinitro-isobutyl toluenel and homologues), which is frequently used as a substitute for musk, or with one of its various derivatives, has therefore been brought to a decision by the isolation of muskone. The "artificial musk" has nothing to do with muskone.

With regard to the remaining odoriferous substances of the musk-secretion, they impair by their penetrating, most unpleasant odour the fine muskone-odour to such an extent, that in the musk it cannot be appreciated at its full value. The examination of these compounds, which are partly of a basic character, has not yet been concluded.

Orris-root, powdered. Since the prices of Florentine roots have advanced about 12 marks per 100 kilos, and this rise appears to be permanent, we have been compelled to increase our quotations for the well-known fine powder for the present by 10 marks. For the rest we beg to refer to what we have said on this subject under the article "Orris Oil".

Peru Balsam. According to Tschirch[1]) the so-called white Peru balsam of Honduras differs considerably from the genuine white Peru balsam obtained from the fruit of *Myroxylon Pereirae.* It contains, besides free cinnamic acid, a solid resin ester of cinnamic acid, and a mixture of liquid resin ester of cinnamic acid with alcohols, which still require further identification. Tschirch considers that the white Peru balsam examined by Thoms and Biltz[2]) is not genuine, as it contained free cinnamic acid and cinnamic acid ester of cinnamon alcohol and phenylpropyl alcohol; the genuine balsam does not contain cinnamic acid at all, but on the other hand coumarin.

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[1]) Schweiz. Wochenschr. f. Chem. u. Pharm. **43** (1905), 238. According to Pharm. Centralh. **46** (1905), 803.

[2]) Zeitschr. d. allg. Oesterr. Apoth. Ver. **58** (1904), 943. Comp. Report April **1905**, 119.

Notes on recent scientific work concerning terpenes and terpene derivatives.

General.

In our last October Report (**1905**, 78) we communicated the results of a study of the laws affecting the composition of a vapour-mixture which is obtained in the distillation of mixtures of liquids. C. v. Rechenberg and W. Weisswange have meanwhile published in the *Journal für praktische Chemie*[1]) the detailed exposition of these researches, under the title of "Distillation of liquids which do not dissolve each other". We would refer to the original work which, in addition to the results already communicated in our Report, contains specially the description of the distillation-experiments with unsaturated oil-vapour in the vapour-mixture.

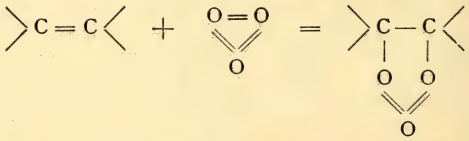
The influence of odours and perfumes on the health of man is discussed in a report which we abstract from the official organ of the German Union of Samaritans[2]): —

"It is long since known that certain substances possessing a strong odour are capable of exerting a powerful influence on the human being. The effect differs no doubt considerably in different individuals, but in particularly sensitive persons it may amount to distinct nervous disturbances. It is an indisputable fact, that perfumes or other strong odours affect in a certain manner the nerves and particularly also the mechanism of the respiration, and can thereby cause, for example, nettle-rash and giddiness. Occasionally odours produce a certain impression on the digestive action, and as a consequence cause nausea, vomiting, excessive salivation, and diarrhœa. It cannot be said that odours, whether pleasant or disagreeable, can actually become the cause of a disease in the usual sense, but they can, by influencing the nerves and interfering with their normal action, disturb certain functions which are necessary for the well-being of man, and thereby reduce the body to a condition which is less capable of resisting the attack of a disease. Of course, there are bound to be wide differences between the individual odours and the various human beings. It is a striking fact that people who are occupied in the scavenging of streets, in canalisation work, in slaughter houses, in tanneries, or such places where they are compelled to inhale unlimited quantities of more or less offensive odours, do not find their general condition impaired thereby in any particular way. A contributor to the *Medical Record* calls to mind that the effluvia of manure were for a long time considered an active remedy against rheumatism, and sometimes are so considered even at this day. A proof that pleasant odours also have really an overpowering effect on the human being is found in the well-known example of the tuberose, of which the presence in a room renders many persons positively unconscious. But a whole series of plants could be mentioned whose odours cause headache, such as the honeysuckle, clove, etc. The fragrance of flowering petunias is said to have caused occasionally slight poisoning. The preparation of decoctions of linseed and also

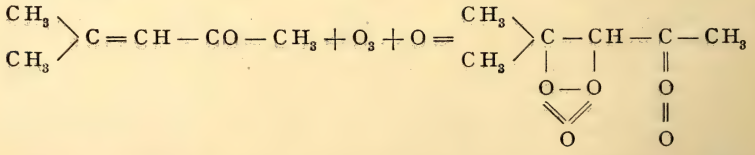
[1]) Journ. f. prakt. Chem. II. **72** (1905), 478.
[2]) *Z*eitschr. für Samariter- und Rettungswesen **12** (1906), 31.

the trituration of cloves, roses, walnuts or coloquints, has often led to cases of unconsciousness. Snake root and bug wort have a very faint unpleasant odour, which, however, occasionally is sufficient to produce headache or even nausea. There are also people who cannot tolerate the smell of freshly ground coffee, which in rare cases is even capable of causing vomiting, although it has a refreshing and appetising action on the olfactory nerves of most people. Tests have now also been made with the view of employing certain odours for medicinal purposes. The perfume of vanilla and heliotrope is said to render valuable services, by soothing very nervous persons. The observation is also said to have been made, that workpeople, both male and female, occupied with the preparation of a perfume, or in its neighbourhood, are generally in a better state of health than other workpeople. But it can hardly be expected that perfumes will ever form an important addition to *materia medica*; they will probably remain as hitherto an object of luxury, although it cannot be denied that at least some of them possess a stimulating action of which the occasional usefulness has nothing to do with fashion or effeminacy".

With due consideration to the existing earlier work, C. Harries[1]) has published the results of his interesting researches "On the action of ozone on organic compounds". The author was led to the more detailed study of the oxidising properties of ozone through observing its action on caoutchouc, which is thereby converted, under suitable conditions, into an oily product. Further experiments then showed, that the manner in which ozone acts on unsaturated hydrocarbons in the absence of water, must be regarded as the absorption of one molecule ozone each by a double-linking present: —



In bodies which, besides an ethylene linking, also contain a carbonyl group, the reaction occurs according to the following diagram, for example: —



These products, called "ozonides", are, as a rule, colourless syrups with an unpleasant suffocating odour; they are partly highly explosive; a few, however, can be distilled *in vacuo* without decomposition. With potassium iodide, indigo solution, and potassium permanganate they show the reactions of peroxides. With concentrated sulphuric acid

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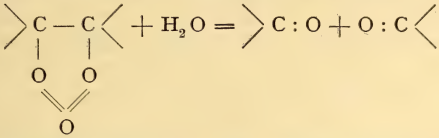
[1]) Liebig's Annalen **343** (1905), 311.

they are decomposed in an explosive manner. When reduced with aluminium amalgam, neither aldehydes or ketones, nor primary or secondary alcohols are formed.

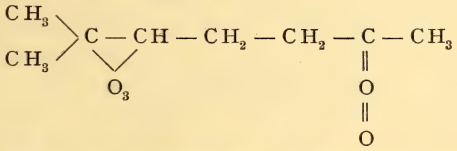
Already with water they split up into aldehydes (or ketones) and hydrogen peroxide, and for this reason they can only be produced in absolutely dry solvents, for example chloroform.



The general behaviour of the ozonides now shows, that they can be employed for the determination of the constitution of unknown compounds. Thus, the action of ozone on oleinic acid and elaidinic acids, supplied the exact proof of the stereo-isomerism of these two acids. Both acids yield ozonides of the formula $C_{18}H_{36}O_6$, which, when heated with water, yield the same products of decomposition, viz., nonylic aldehyde (or nonylic acid) and the semi-aldehyde of azelainic acid (or azelainic acid respectively). The semi-aldehyde, when exposed to the air, very rapidly combines with oxygen, and could therefore not be isolated as such.

Pulegone and pinene formed ozonides whose products of decomposition are still being studied. Among others, the following ozonides have also been produced:

Methylheptenone ozonide,



It is formed when methylheptenone is ozonised, as a water-white syrup; $d_{19°}$ 1,1380.

Citronellal ozonide, $C_{10}H_{18}O_5$; a water-white syrup, non-explosive; $d_{21°}$ 1,0746; when distilled *in vacuo*, it is split up in oxygen and citronellal.

Citral ozonide $C_{10}H_{16}O_5$; a water-white syrup; $d_{21°}$ 1,1486.

Oenanthyl peroxide $CH_3(CH_2)_5CH{=}O{=}O$; from heptylic aldehyde and ozone. When shaken with ice water it reproduces heptylic aldehyde.

Balbiano has submitted[1]) in the form of a "memoria" to the Reale Accademia dei Lincei, of Rome, his studies on the action of

[1]) According to reprint kindly sent to us.

aqueous mercuric acetate solutions on olefinic compounds, published by him jointly with Paolini, Tonazzi, Cirelli, and others. As we have already reported on the most important parts of the various works[1]), we content ourselves in this place with a reference to the detailed comprehensive treatment of the "memoria"; we only wish to add, that the glycols $R \cdot CHOH \cdot CHOH \cdot CH_3$ formed by the action of mercuric acetate on phenol ethers with propenyl side chain (anethol, isosafrol, methyl isoeugenol), on splitting off water by means of zinc chloride, yield aldehydes. There are not formed (as was at first supposed) the substituted hydratropic aldehydes $R \cdot CH(CH_3) \cdot CHO$ of Bougault[2]), as the derivatives (oximes, semicarbazones, acids) show different melting points, but hydrocinnamic aldehydes of the formula $R \cdot CH_2 \cdot CH_2 \cdot CHO$.

Bibliographical notes.

O. Aschan has published a large work under the title "Chemistry of the alicyclic compounds"[3]). In this class of bodies, the terpenes and their derivatives, as is well known, occupy the largest space; the book, however, does not confine itself to these, but deals with all hydrated cyclic bodies which have become known up to the present, from trimethylene up to completely hydrated picene. In the general part of this work, the theoretic relations of the alicyclic bodies towards each other have been reproduced in historical order, the fundamental work of v. Baeyer on the hydrobenzene derivatives, his theory of tension, and next in detail the more recent researches on terpenes and camphors commencing with Wallach's work. Separate chapters have been devoted to the influence of the ring-formation on the chemical and physical characteristics of the alicyclic compounds, and also to the stereo-chemistry of these bodies, a field in which not much work has been done up to the present. The special part shows first of all the general manner of formation of the individual hydroaromatic hydrocarbons, alcohols, aldehydes, ketones, acids, and their derivatives, next these bodies themselves, in the order of the number of carbon rings and of the carbon atoms forming them, whereby naturally the terpenes and camphors receive the most detailed treatment.

In this monograph, in which the extremely rich and widely dispersed material is arranged most conveniently and easy of survey, the author has, in his own particular working sphere, created a work which obtains

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[1]) Report April **1903**, 83; April **1904**, 100.

[2]) Thesis, Paris, 1902. Report April **1903**, 11. Comp. the present Report page 132.

[3]) Chemie der alicyklischen Verbindungen. Brunswick 1905. Fr. Vieweg & Sohn.

its special value from the criticism interspersed in it, and which will be most welcome particularly to those who wish to make themselves acquainted with the historical development and with the relationship between the individual bodies.

We only wish to refer here to the work published by J. W. Brandel[1]): "The Volatile Oils 1904", as the interesting parts of the contents have already been communicated in these Reports in the most diverse places.

Physical notes.

Some time ago Haller[2]) already pointed to the increase in the rotatory power of active bodies, which is caused by attaching a radical such as particulary benzylidene, by means of a double-linking. In their last work Haller and March[3]) compare the following partly new bodies and their rotatory powers with each other: benzylidene camphor; hexahydrobenzylidene camphor, colourless crystals of the melting point 49° obtained by condensation of hexahydrobenzaldehyde with camphor sodium which had been produced from camphor by means of sodium amide in ethereal solution; benzyl camphor; hexahydrobenzyl camphor obtained by reduction of hexahydrobenzylidene amalgam, boiling point 192° at 24 mm. pressure; œnanthyl camphor, produced by the action of heptyl iodide on camphor sodium, a colourless oil of the boiling point 190° at 25 mm. pressure; œnanthylidene camphor by brominating œnanthyl camphor and splitting off the hydrobromic acid by means of diethylaniline; boiling point 180° to 182° at 20 mm. pressure.

Specific rotatory power:

a) of the unsaturated bodies

benzylidene camphor	$[\alpha]_D + 425° 11'$,
hexahydrobenzylidene camphor	„ $+ 131° 39'$,
œnanthylidene camphor	„ $+ 136° 40'$;

b) of the saturated bodies

benzyl camphor	$[\alpha]_D + 144° 00'$,
hexahydrobenzyl camphor	„ $+ 55° 07'$,
œnanthyl camphor	„ $+ 51° 13'$.

By this comparison, it is clear that the specific rotatory power of the new hydrated bodies is much lower than that of the corresponding benzene compounds. The rotation of the saturated alkyl derivatives is lower than that of the unsaturated derivatives from which

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[1]) Pharm. Review **23** (1905), 321, 339 and 376, **24** (1906), 14 and 39.
[2]) Compt. rend. **140** (1905), 1626.
[3]) Compt. rend. **142** (1906), 316.

they are derived. The nature of the saturated side-chains C_6H_{11} and C_6H_{13}, whether they be alicyclic or aliphatic, does not appear to have any appreciable effect on the rotatory power. In benzylidene camphor and its anologues, such as benzyl camphor, it must therefore be the character of the unsaturated benzene nucleus which exerts its influence on the rotatory power of the asymmetric molecule to which it is attached.

Pharmacologico-physiological notes.

A paper by E. Sack[1]) on odoriferous substances and olfactory sensations, contains interesting information which we can only reproduce here in a few words, as we are only in possession of a short report on the subject. What is usually understood under the expression odoriferous substances, is, chemical individuals which are employed for perfuming objects of use. An exact scientific definition, such as for example that of the idea "dye-stuff", cannot be given of the idea "odoriferous substance". They might possibly be designated as carbon compounds which under certain conditions, whereby a chemical change is excluded, emit a definite characteristic odour. It has often been attempted to group odoriferous substances, like colouring matters, together from certain chemical points of view [Rupe and Majewski[2]), Klimont[3])], but when such a group is submitted to a more thorough study, there are found, besides much which is lawful and regular, so many irregularities and exceptions, that it is impossible to carry the principle through. The relationship between the character of the odoriferous substance and the chemical constitution is usually not very easily recognisable, and is frequently of a very complex nature. Above all, one should not be led away too easily by theoretical speculations, as statements in literature on odour-emitting bodies are afterwards very often found to be unreliable. This may possible in part be explained by the fact that many people are unable to smell correctly, and partly by this, that many bodies which are looked upon as chemically pure, do not possess a pure odour. Occasionally again, odoriferous substances in solid or concentrated form do not possess the characteristic odour which they have when properly diluted. It also happens sometimes that the odour of a body in concentrated form differs entirely from that of the greatly diluted body, so much so, that they might be taken for different bodies. It is well know that the strength of the odour in many substances does not at all stand in simple relation to the degree of concentration or dilution in which the substances occur. Even

[1]) Chem. Ztg. **29** (1905), 1298.
[2]) Berl. Berichte **33** (1900), 3401.
[3]) Klimont, The synthetic and isolated aromatics, p. 7.

products which are closely allied, in chemical constitution and composition, may differ completely from this point of view. These are all peculiarities which cannot possibly be compared with the conditions prevailing for colouring matters. And for this reason it will hardly ever be possible to speak of a theory of odoriferous substances, in like manner as is now done of a theory of dye-stuffs. The paper concludes with a discussion on the manner in which the sensation of odour is accomplished, and on the methods by which odours are tested and compared with each other. In the last-named work a good memory for the individual odours is very useful, and this can be very much perfected by constant practice.

From Vandevelde[1]) originates a biological method for the determination of the toxic action of chemical compounds, which has assisted in the examination of alcohols and of essential oils and some of their constituents[2]). The principle of his method is based on this, that essential oils in definite quantities bring about hæmatolysis in defibrinated bullock's blood floating in the proportion of 5 per cent. on normal solution of common salt. The test is made in this manner, that to 2,5 cc. of a 5% suspension of defibrinated bullock's blood in normal solution of common salt (0,9% NaCl), are added together 2,5 cc. of a mixture of normal solution of common salt and of a solution of 0,05 gm. of the oil to be examined, in 100 cc. of 50 per cent. alcohol (with 0,9% Na Cl). According to the content of essential oil or of the 50% aqueous-alcoholic solution, in the last-named 2,5 cc. mixture, hæmatolysis occurs sooner or later in the total mixture (5 cc.), and by eliminating the known hæmatolytic action of the alcohol, the share of the essential oil in the hæmatolysis can be determined numerically, and its relation as isotoxic value to the unit of weight of alcohol fixed. According to this, the so-called "fruit oils", strawberry, raspberry, apple and other oils, possess the most feeble hæmatolytic action, 4,78 gm. as compared with 100 gm. absolute alcohol; the next in the series are peach and bitter almond oils, and benzaldehyde, with 2,33 gm., nitrobenzene and carvone with 1,10 gm., whilst finally anethol, anise oil, and star-anise oil reach the highest isotoxic value with 0,20 gm. Vandevelde hopes to be able to base a new bio-chemical method for the determination of essential oils in alcoholic beverages on his process.

We feel bound to qualify the name "fruit oils" as indistinct, inasmuch as it is not clear whether it applies to the natural oils, or

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[1]) Chem. Ztg. **29** (1905), 975.

[2]) Bull. de l'Assoc. Belge des chimistes **17** (1903), 269; 208. Report October **1904**, 102.

to the artificial fruit essences (esters of certain fatty acids). In this connection it is curious that peach"oil" does not take its place among the "fruit oils", but on the contrary shows the isotoxic value of benzaldehyde, whilst on the other hand cognac oil, natural and artificial, figure at the other end of the series with 0,28 and 0,22 respectively. In the case of bitter almond oil, it might not be altogether unimportant, whether it is used free or not from hydrocyanic acid. It appears questionable whether this method is suitable as a method of determination, in view of the frequently extremely minute quantities of essential oils in liqueurs, especially when it is taken into consideration that in the majority of liqueurs it is a question of mixtures of essential oils.

Galewsky[1]) recently observed a case, in which a lady suffered from inflammation with red spots like nettle-rash, accompanied by severe itching, on the parts of the neck which were not covered by the dress, and which was clearly due to the fact that she had been staying in a room which was decorated with eucalyptus shrubs. The same eruption appeared already after half an hour in a girl who had rubbed the shrubs on the skin.

Phyto-physiological notes.

In a previous work Charabot and Hébert[2]) have studied the influence exerted by the development of the inflorescences on the essential oil of the green organs of sweet basil (*Ocimum basilicum*), and a recent communication of the same authors[3]) deals with the effect of the blossoms which perform their function, on the odoriferous substances.

A bed of sweet basils was divided in two parts, of which one contained the experimental plants, and the other the control plants. From the former, the newly formed inflorescences were from the commencement of the flowering season removed every day and weighed, and extracted with petroleum ether, in order to determine the total quantity of essential oil produced. At the commencement of the experiments, a trial cut was made, and the state of development of the plants, their oil-content, and the composition of the oil determined. When the fructification was completed, the control plants were cut, and the green parts distilled and the inflorescences extracted with petroleum ether. The extract was then submitted to distillation with water vapour. On the same day the experimental plants were also distilled, and the same took place with the extract obtained during

[1]) Dermatol. Zeitschr. **1905** No. 1; According to Pharm, Centralh. **46** (1905), 968.
[2]) Compt. rend. **138** (1904), 380; Bull. Soc. Chim. III. **31** (1904), 402.
[3]) Compt. rend. **141** (1905), 772; Bull. Soc. Chim. III. **33** (1905), 1121.

the experimental period by means of petroleum ether from the blossoms cut off. A comparison of the results obtained showed the following: The removal of the inflorescences causes a considerable increase in the weight of the plant, up to 39% of the normal weight. The quantity of oil of any individual plant has almost doubled, the increase amounting to up to 82% of the normal production. The older inflorescences which have accomplished their function have retained less odoriferous matter than the inflorescences cut off had taken away. The absolute weight of the oil remaining behind in the green parts of each plant has increased, but this increase is not proportionate to their development. This is due to the fact that, whilst in the control plants after completed fructification a certain quantity of oil returns[1]) to the parts containing chlorophyl, this return cannot take place in the experimental plants, as they have been systematically deprived of their inflorescences. On the other hand, the authors found that the comparative quantity of oil is also larger in the experimental plants, which may be explained thus, that in the inflorescences which have remained on the plants, essential oil has been consumed in the fructification process[2]).

The observations made also explain why the peppermint[3]) which has been changed by the stings of insects and which has lost the capacity of developing blossoms, shows a considerable increase in the development of the green organs and an important augmentation in the oil production.

On the formation and distribution of essential oil in the sweet orange during its development, Roure-Bertrand Fils[4]) have made researches of which the result may be summed up in the following: The formation of essential oils is brisker in the young organs of the plant than in those which are already fully developed. The stalk is noticeably poorer in odoriferous substances than the leaf, and it especially contains considerably less citral. The quantity of essential oil remaining behind in the stalk diminishes constantly.

Bourquelot and Danjou[5]) have continued their examinations of the glucoside contained in the common elder (*Sambucus nigra* L.), to which we referred in our last Report[6]). 1 Kilo fresh leaves, macerated

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[1]) Charabot and Laloue, Compt. rend. **139** (1904), 928 and **140** (1905), 667. Comp. Report October **1905**, 90.

[2]) Compt. rend. **140** (1905), 667. Comp. Report October **1905**, 90.

[3]) Comp. the report under Peppermint oil, p. 54.

[4]) Reports of Roure-Bertrand fils, Grasse, October **1905**, 21.

[5]) Journ. de Pharm. et Chim. VI. **22** (1905), 210.

[6]) Journ. de Pharm. et Chim. VI. **22** (1905), 154. Report October **1905**, 110.

with water with emulsin added, yielded 0,142 gm. hydrocyanic acid. The alcoholic extract from 1 kilo leaves, after removal of the alcohol and substitution of the latter by water after invertin and emulsin had been added, yielded 0,156 gm. hydrocyanic acid. In the fresh leaves and also in the other organs of common elder, the authors detected invertin; the blossoms contain most of it, whilst the young fruit appears to have the smallest content. Small quantities of emulsin are also present in the leaves, blossoms, and fruit. In addition to two varieties of *Sambucus nigra*, which also contained the glucoside, the authors examined *Sambucus racemosa* L. and *Sambucus Ebulus* L., but in neither of these could a glucoside be detected. But possibly the latter may contain another body which can be split up by emulsin. In the further course of the examination, Bourquelot and Danjou[1]) succeeded in obtaining in crystalline from the glucoside which they had hitherto not been able to produce in the pure state. It crystallises in long colourless needles, is odourless and has a slightly bitter taste. It is readily soluble in water, cold alcohol, and acetic ether, almost insoluble in ether; it softens at 149° and melts at 151 to 152°. It is optically active ($[\alpha]_D$ — 76,3°), does not lose weight when heated to 100°, and does not reduce Fehling's solution. The hitherto unknown glucoside which resembles amygdalin, and which the authors have named sambunigrin, is split up by emulsin into glucose (61,28%), hydrocyanic acid (8,61%), and benzaldehyde; it appears to be isomeric with the amygdonitril glucoside $C_{14}H_{17}NO_6$ of E. Fischer. In a further work Bourquelot and Danjou[2]) describe in detail the production, purification and properties of sambunigrin. It should still be mentioned that the glucoside can also be split up by the ferment of *Aspergillus niger*, and that, as a matter of fact, the above-mentioned formula $C_{14}H_{17}NO_6$ belongs to it.

Stimulated by this work, L. van Italliе[3]) has again taken up his earlier investigations on the presence of hydrocyanic acid in plants and he was not only able to confirm the results of Bourquelot and Danjou, but also became acquainted with a new occurrence of hydrocyanic acid. In the leaves of *Thalictrum aquilegifolium* L. he detected in 100 gm., 0,05 to 0,06 gm. hydrocyanic acid, in 142 gm. twigs he found 0,0044 gm., but in 200 gm. roots no trace of hydrocyanic acid at all. The leaves of *Thalictrum flavum* L., *Thalictrum minus* L., and *Thalictrum glaucum* did not contain hydrocyanic acid. The acid originates from a glucoside which, like the phaseolunatin discovered by Dunstan and Henry in *Phaseolus lunatus* L., can be split up

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[1]) Ibidem p. 219. Compt. rend. **141** (1905), 598.
[2]) Journ. de Pharm. et Chim. VI. **22** (1905), 385.
[3]) Ibidem p. 337.

into acetone and hydrocyanic acid. Apart from the glucoside, the author detected in *Thalictrum aquilegifolium* an enzyme, which is capable of decomposing both the glucoside found and amygdalin.

Another new glucoside, prulaurasin, has been isolated by H. Hérissey[1]) from the leaves of the cherry laurel (*Prunus laurocerasus* L.). By extracting the leaves with boiling water, evaporating the bulk of this *in vacuo,* diluting the residue with alcohol, filtering, driving off the alcohol *in vacuo*, and purifying the residue, he obtained the body in a crystalline state. It crystallises in thin colourless needles, has a slightly bitter taste, melts at 120 to 122°, is readily soluble in water, alcohol, acetic ether, almost insoluble in ether, and turns the plane of polarised light to the left ($[\alpha]_D$ — 62,69°). Emulsin splits up prulaurasin into hydrocyanic acid (8,59 %), glucose (61,24 %), and benzaldehyde. It has the formula $C_{14}H_{17}NO_6$, and is isomeric with the amygdonitril glucoside of E. Fischer[2]) and the above-mentioned sambunigrin of Bourquelot and Danjou. It differs from these two by its solubility, its melting point, and its optical rotatory power.

According to L. Guignard's[3]) examinations, the red currant bush (*Ribes rubrum* L.) also contains small quantities of a glucoside splitting off hydrocyanic acid. From 100 gm. leaves were obtained: in June when the currants were still green, 0,0035 gm. hydrocyanic acid; a few weeks later, when they were ripe, 0,0026 gm., and in the beginning of August only 0,0015 gm. In 100 gm. of the young branches which only contained little chlorophyl, only small quantities could be detected, and in an equal weight of roots and the ripe fruit no trace of hydrocyanic acid could be found. Of other species of *Ribes, Ribes aureum* Pursh., behaved the same as *Ribes rubrum;* the quantity of glucoside was only smaller. The leaves of *Ribes nigrum* L., *Ribes uvacrispa* D. C., *Ribes sanguineum* Pursh., *Ribes multiflorum* Kit., *Ribes subvestivum* Hook. et Arn., *Ribes prostratum* L'Hér., and *Ribes Gordonianum* Lem., yielded no hydrocyanic acid. In the leaves and twigs containing glucoside, and in the roots and fruit free form glucoside of *Ribes rubrum* and *Ribes aureum,* the author detected emulsin, and the like in the species *Ribes nigrum* and *Ribes uvacrispa* which contain no glucoside at all. Of seeds, only those of *Ribes rubrum* and *Ribes nigrum* were examined, and in them the presence of emulsin was proved.

The examination of prulaurasin compelled Hérissey[4]) to determine small quantities of benzaldehyde. For the separation of the

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[1]) Compt. rend. **141** (1905), 959, and Journ. de Pharm. et Chim. VI **23** (1906), 5.
[2]) Berl. Berichte **28** (1895), 1508.
[3]) Compt. rend. **141** (1905) 448.
[4]) Journ. de Pharm. et Chim. VI. **23** (1906), 60.

aldehyde he employed phenylhydrazin, filtered off the phenylhydrazone formed, and after drying weighed it. He made use of pure crystallised amygdalin for controlling the process. A weighed quantity of the last-named substance was mixed with 60 cc. water and with sufficient emulsin to complete the decomposition of the glucoside in 2 to 3 days at 15 to 20°. He then distilled 50 cc. off form the mixture, and mixed the distillate with 50 cc. of a solution which contained in 100 cc., 1 cc. freshly distilled phenylhydrazin and 0,5 cc. glacial acetic acid, so that a large excess of phenylhydrazin was present. He then heated for 20 to 30 minutes in a boiling water bath, and after 12 hours filtered the phenylhydrazone formed in a Gooch's crucible, washed with 20 cc. cold water and dried in a vacuum exsiccator. In five estimations with constantly diminishing quantities of amygdalin, he thus founed in amygdalin an increasing content of 21,09 to 22,5% benzaldehyde, whilst theoretically 23,19% are required. Hérissey recommends that in carrying out the determination only such quantities of benzaldehyde should be used, as yield 0,1 to 0,25 gm. phenylhydrazone, and for the rest to follow the course indicated for amygdalin.

A contribution to the knowledge of the essential oils of the Hepaticæ by Karl Müller[1]) is intended to supply a further proof that the view of Pfeffer[2]) which at present is still generally accepted, that the oil bodies of the Hepaticæ consist chiefly of fatty oil with small admixtures of protein substances and water, is erroneous. The author examined only Jungermanniaceæ, viz., —

1. *Mastigobryum trilobatum* L. This hepatica when dried in the air loses 90% of its weight, and yields on rational steam-distillation 0,93% of the dry substance of an orange-yellow essential oil, which resembles in the odour sandal and cedarwood, but at the same time reminds of the odour of pine-needles $d_{15°}$ 0,945 to 0,947 (a sample distilled with a bad yield had $d_{15°}$ 0,975); $[\alpha]_D$ + 12,88° (determined with undiluted oil); saponification number 5,4. On saponification, an acid mass, semi-solid at 16°, was obtained, which yielded a white lead salt, soluble in ether. The bulk of the oil boiled at 260 to 270°. The distillate had a blue-green colour, $d_{20°}$ 0,946; $[\alpha]_D$ + 25,59°; it contained 87,06% C and 12,65% H. When this principal fraction was oxidised with chromic acid and glacial acetic acid, a body C_{10} H_{16} O was obtained (boiling point 260°), and for this reason the author attributes to the crude material the terpene formula C_{10} H_{16}. The last runnings of the oil (boiling point 270

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[1]) Zeitschr. f. physiol. Chem. **45** (1905) 299 Accord. to Chem. Centralbl. **1905**, II, 768. Comp. also Report April **1904**, 106.

[2]) The oil bodies of the hepaticae, "Flora" **1874**, No. 1 to 3.

to 285°) contained 5,4 % oxygen, and had the specific rotation $[\alpha]_D$ + 42,21° (determined in 3,9 per cent. alcoholic solution).

2. *Leioscyphus Taylori* Hook. This moss dried at 100° and pulverised, yielded 1,6 % viscid, blue-green, essential oil with a very intense, persistent, peculiar odour, and a very unpleasant taste; $d_{20°}$ 0,978 and 0,986; $[\alpha]_D$ — 3,44° (determined in 9,03 per cent. alcoholic solution); saponification number 11,4. The analyses of the fraction of the boiling point 260 to 265°, d 0,937, $[\alpha]_D$ — 22° (?) agreed with a sesquiterpene alcohol $C_{15}H_{26}O$. The fraction of the boiling point 265 to 278° appears to contain a terpene $C_{15}H_{24}$. The fraction of the boiling point 280° to 290° ($[\alpha]_{white}$ + 26,88°) contains a sesquiterpene alcohol $C_{15}H_{26}O$. Solid benzoyl compounds could not be obtained from either alcohol.

3. *Madotheca levigota* Schrad. The moss dried in the air yielded 0,9 % of a comparatively mobile, orange-yellow oil with a pleasant odour; $d_{16°}$ 0,856; $[\alpha]_D$ + 72,74°; saponification number 5,56. The peppermint-like taste of the moss does not originate from the essential oil. The fraction of the boiling point 150 to 160° (17 mm. pressure) $d_{15°}$ 0,968, $[\alpha]_D$ + 132,23°, boils at atmospheric pressure with decomposition at 280°, and contains an alcohol $C_{10}H_{18}O$.

4. *Alicularia scalaris* Corda. The oil of this hepatica is lemon-yellow, and reminds in the odour of the fragrance of the forest; $d_{15°}$ 0,965; $[\alpha]_D$ — 33,49°.

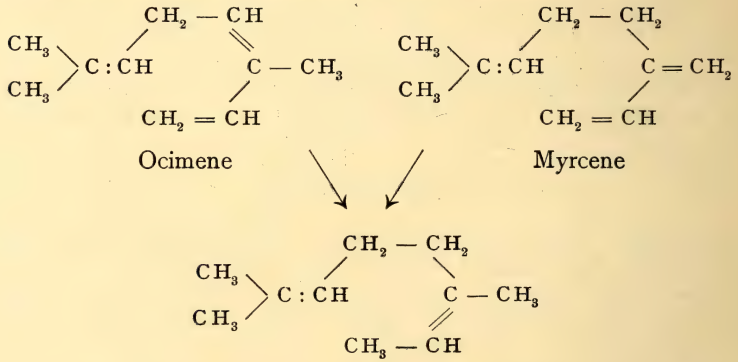
Hydrocarbons.

Myrcene, Ocimene. The number of the olefinic terpenes which have become known up to the present is but small. The member of this class first described in the year 1891, the artificially produced anhydrogeraniol of Semmler, has not been examined further; but there are numerous communications in existence dealing with the two olefinic terpenes myrcene and ocimene which occur naturally.

Enklaar[1]) has set himself the task of clearing up the relationship between these two bodies. The ocimene was produced from the leaves of *Ocimum basilicum* L., in a yield of 0,37 %, and obtained by suitable treatment as an oil of the specific gravity 0,8031, $n_{D18°}$ 1,4857. The myrcene, which we had placed at the author's disposal for the purpose of this examination, had after purification $d_{15°}$ 0,8013, $n_{D19°}$ 1,4700. Whilst ocimene, under unfavourable conditions, hardly changed after 4 years, myrcene had almost entirely become resinified after 2 years, in spite of the fact that light and air had been excluded. The two terpenes, which were beyond doubt identified as different substances,

[1]) Over Ocimen en Myrceen, eene bijdrage tot de kennis van de aliphatische terpenen. Thesis, Utrecht, **1905**.

yielded on reduction with sodium and alcohol the same product of hydration, i. e., a hydrocarbon $C_{10}H_{18}$ with two double linkings, and had the following constants: boiling point 166° to 168° (at 761 mm. pressure), $^{n}D17^{\circ}$ 1,451, molecular refraction found 47,62, calculated 47,34. The specific gravity of the dihydro-terpene from ocimene was 0,779; the one obtained from myrcene was higher, namely 0,785, probably owing to the presence of some unchanged myrcene. The identity of the two products of reduction was further shown by the identity of the tetrabromides of the melting point 88° produced from them. It is therefore accepted as an established fact, that both ocimene and myrcene are olefinic terpenes with three double linkings, of which one can be saturated off by hydration, and the two others by the addition of bromine. Different oxidation experiments with ocimene yielded as characteristic compound malonic acid, and from this, as also from the results of the redaction on the strength of Thiele's views concerning the so-called conjugated double-linkings Enklaar deduces for the two terpenes the following formulæ: —



Ocimene Myrcene

Dihydroocimene (or dihydromyrcene).

By hydration according to Bertram-Walbaum's method, there was formed from myrcene the optically inactive alcohol $C_{10}H_{18}O$, myrcenol, which Power and Kleber consider identical with linalool, but which is thought to be different from the latter by Barbier, Semmler and others. By comparison with the phenyl urethane of linalool which was first produced in our laboratory[1]), and which he examined particularly for its optical activity, Enklaar demonstrated that the two alcohols are different, although the melting points of their phenyl urethanes lie only 2 to 4° apart. Myrcenol phenyl urethane melted at 68°, the urethane of the optically active linalool

[1]) Report October **1902**, 70.

at 64°, and of the racemic linalool at 66°. For linalool, Tiemann-Semmler's formula could be confirmed. The corresponding ocimenol yielded a phenyl urethane of the melting point 72°.

When heated in a reflux-condenser, ocimene is converted (according to van Romburgh) into an isomeric "alloocimene"; Enklaar considers the latter a geometric-isomeride, as it yields on reduction the same dihydro product as ocimene. Attempts made to arrive at the corresponding alcohol by hydration with glacial acetic acid and sulphuric acid failed and led back again to ocimene.

Pinene. Concerning this terpene, Kondakow[1]) gives a historical retrospect of the development of the formulæ drawn up for pinene by Kannonikow, Wallach, Bredt, v. Baeyer and Wagner. But while the structure of pinene itself has now become clear, this is not yet the case with regard to the reaction-mechanism of the principal conversions. A distinction must be made whether the reaction occurs with the double-linking, or with the diagonal linking of pinene. Thus, in the oxidation into pinene glycol and into pinol, the latter appears to be split asunder and the double linking to remain intact. In view of the spatial arrangement of the pinene molecule, a direct conversion from the glycol to pinol with loss of water might be accepted. On the other hand, in the treatment with acids, in attaching HCl, etc., the bridge linking remains intact, and the reactions takes place with the double linking. Kondakow includes in this the formation of pinene hydrochloride and its isomerides, of pinene dibromide, and also of terpineol, whereby SO_4H_2 is said to attach itself to the double linking, with erection (Kondakow says not quite correctly "splitting-off") of the isopropyl-group, and in which subsequently the ester and finally the alcohol itself is formed[2]). According to Kondakow, the formation of the terpineol derivatives occurring naturally results in a similar manner. The occurrence of isomeric additional compounds is explained partly by re-grouping of the additive atom-arrangements in the finished product, and partly by their entrance at various places in the picean ring. This appears to be proved by the behaviour of the as yet little examined alcohol pinanol [pino campheol][3]).

With regard to the behaviour of pinene while being brominated, and the occurrence of cyclene, the opinions have not yet become

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[1]) Chem. Ztg. **29** (1905), 1225.

[2]) Kondakow's ideas about the reaction-process are, in our opinion, not very clearly expressed.

[3]) Whether, as Kondakow supposes, a migration of the carbon linkings in the HCl addition product of this alcohol, with formation of bornyl chloride and Fenchyl chloride, actually takes place, will have to be proved by the further experiments which are announced.

settled, as the views of Wagner, Semmler and Kondakow on the course of the reaction have not been strictly proved, and contradict each other.

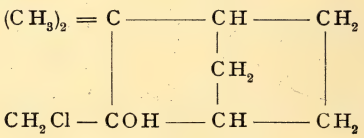
In distilling the xanthogenic acid ester of Wallach's pinocampheol[1]) according to the usual method, A. Tschugaeff and A. Esche[2]) observed between 180° and 190° a very energetic decomposition. The reaction took place according to the following equation:

$$C_{10}H_{17}O \cdot CS \cdot SCH_3 = C_{10}H_{16} + COS + CH_3SH.$$

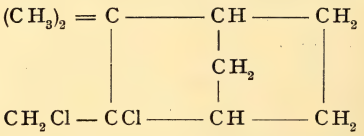
The hydrocarbon formed, after distillation in a current of vapour, shaking with potash liquor, and purification over sodium, was found to be pure pinene of the boiling point 155° to 156°. The melting point of its nitrosochloride was found at 103°.

Camphene. According to K. Slawinski's[3]) examinations camphene combines with hypochlorous acid, with formation of the following products:

1. Camphene glycol chlorhydrin



2. The chloride $C_{10}H_{16}Cl_2$ of the melting point 139° to 140°,



3. A mixture of three isomeric monochlorides $C_{10}H_{15}Cl$, which consists of camphene monochloride, cyclene monochloride, and an unknown chloride.

From his examination the author draws the conclusion that the structure of isoborneol and camphene is the same.

Phellandrene. J. Kondakow and J. Schindelmeiser[4]) have attempted to produce phellandrene synthetically from carvomenthene.

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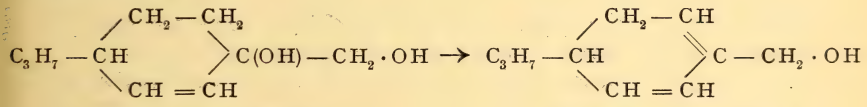
[1]) Liebig's Annalen **300** (1898), 288. Report October **1898**, 54.
[2]) Accord. to Chem. Ztg. **29** (1905), 1189.
[3]) Bull. Intern. Acad. Cracovie **7** (1905), 491. Acc. to Chem. Ztg. Repert. **29** (1905), 378.
[4]) Journ. f. prakt. Chemie II. **72** (1905), 193.

They converted carvomenthene, according to Reychler's method, into tertiary carvomenthol, and the latter, through the chloride (boiling point 83,5 to 84,5° at 12 mm. pressure, $d\frac{20°}{4°}$ 0,932) into tertiary carvomenthene (boiling point 174 to 176°; $d\frac{20°}{4°}$ 0,811; n_D 1,45709). From this the dibromide was produced, and from the last-named body was obtained, by the action of alcoholic potash, a hydrocarbon of which the bulk boiled at 175° to 180° ($d\frac{20°}{4°}$ 0,825; n_D 1,46693), whilst the smaller portion ($d\frac{20°}{4°}$ 0,828; n_D 1,4673) passed over at 180° to 185°. Both fractions are inactive. The authors believe that their hydrocarbon (which is not uniform) either has the constitution of Semmler's[1]) phellandrene, or is isomeric with it. In order to compare it with natural phellandrene, the authors produced the as yet little known halogen addition products of d-phellandrene from oil of water fennel. By the action of hydrochloric acid in a solution of glacial acetic acid, they obtained a product which could by fractionating be split up into a solid monochloride $C_{10}H_{17}Cl$ (boiling point 86° at 11 mm. pressure, melting point about 110°; dextrorotatory) and a liquid dichloride $C_{10}H_{18}Cl_2$ (boiling point 122,5 to 125° at 16 mm. pressure; $d\frac{20°}{4°}$ 1,006; n_D 20° 1,48516).

According to Wallach's[2]) examinations, β-phellandrene of water-fennel oil is converted by oxidation with potassium permanganate into a glycol which, by loss of water, yields tetrahydrocuminic aldehyde. Wallach[3]) has now, in addition to this body, also observed the presence of dihydrocuminic alcohol, which can also be formed when water is split off:



β-phellandrene glycol — dihydrocuminic alcohol

As, besides β-phellandrene, tetrahydrocuminic aldehyde is present in water-fennel oil itself, Wallach[4]) endeavoured to determine whether the readily oxidisable hydrocarbon could be converted by oxidation with free oxygen in the presence of water, into the aldehyde mentioned above. β-Phellandrene was shaken in sunlight with an equal quantity of water, in a flask filled with oxygen. There was then obtained, besides 35 to 36% of unconverted phellandrene, not the expected

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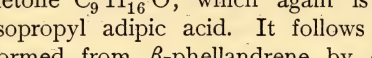
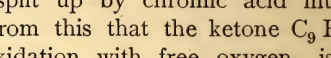
[1]) Berl. Berichte **36** (1903), 1749.
[2]) Liebig's Annalen **340** (1905), 1. Report October **1905**, 97.
[3]) Liebigs Annalen **343** (1905), 37.
[4]) Ibidem p. 29.

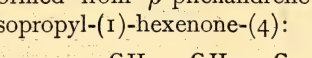
tetrahydrocuminic aldehyde, but 5 to 10% (calculated as semicarbazone) of a ketone $C_9H_{14}O$ (boiling point 103 to 106° at 15 mm. pressure, 220 to 224° at atmospheric pressure; d 0,9387; $n_{D26°}$ 1,4788), which possessed an odour greatly resembling that of the aldehyde and whose semicarbazone melts at 183 to 184°. The unsaturated ketone combines with sodium bisulphite, and in alcoholic-ammoniacal solution with sulphuretted hydrogen into a sulphur compound which melts at 121 to 122°. It can be reduced with sodium and alcohol or moist ether to a saturated alcohol, which can be oxidised to a saturated ketone $C_9H_{16}O$, which again is split up by chromic acid into β-isopropyl adipic acid. It follows from this that the ketone $C_9H_{14}O$ formed from β-phellandrene by oxidation with free oxygen, is Δ_2-isopropyl-(1)-hexenone-(4):



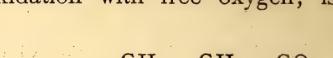
β-phellandrene



isopropylhexenone



isopropylhexanone



β-isopropyladipic acid

The progress of the oxidation shows that the oxidation of unsaturated compounds by means of free oxygen proceeds in a totally different manner from that with potassium permanganate. Whereas, if the last-named agent is employed, it commences with the addition of hydroxyls, in the "autoxidation" superoxides are first of all formed, with absorption of oxygen. Of both oxidising agents the semicyclic linking is more readily attacked than the purely cyclic one.

Isopropyl-(1)-hexenone-(4) could (as Wallach surmised) also be obtained from the above-named glycol by oxidation with chromic acid.

The odour of the ketones produced by Wallach induces him to believe that the position of the oxygen towards the isopropyl-group influences the odour of cyclic ketones in such manner, that the ortho-position brings about the odour of menthone, the meta-position that of carvone, and the para-position a cuminal-like odour.

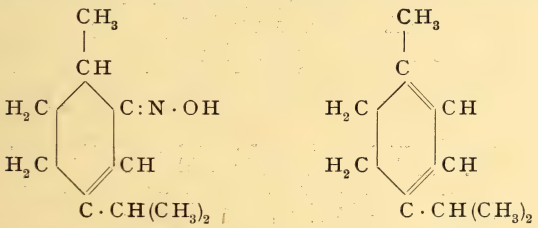
The base[1]) previously obtained by reduction of nitro-β-phellandrene of which it was still doubtful whether it was a di- or a tetrahydrocuminylamine, was now recognised as identical with the tetrahydro base which can be produced from tetrahydrocuminaldoxime.

Semmler's proposal, to designate the terpenes which, like-β-phellandrene, contain a semi-cyclic :CH_2-group, as *pseudo* terpenes, is

[1]) Liebig's Annalen **340** (1905), 8; Report October **1905**, 97.

not accepted by Wallach[1]), as just these terpenes are not "false", but are specially characteristic. But as the need is felt to give a name to this : CH_2-group, which for example is present in limonene, carvone, citronellal, isopulegone, and the phenols examined by Auwers and Zincke, he calls it "methene".

Terpinene. T. Amenomiya[2]) supplies a contribution to the constitution of terpinene with the continuation of his studies[3]) of the nitro-nitrosite of this terpene. If 5 gm. of this compound with 50 cc. 75 per cent. alcohol and 15 gm. zinc dust are heated to boiling, a brisk reaction takes place, with development of nitrous acid. When water is added, a syrup is precipitated, which finally becomes solid. When distilled in a current of steam, a colourless oil passes over which soon becomes crystalline. The product purified with methyl alcohol melts at 91 to 92°, and proved to be carvenone oxime. The melting point of the semicarbazone of the carvenone obtained from it lies at 204°. In the same manner terpinene nitrosite can be reduced. According to this result one feels inclined to believe that terpinene must be the carvenene which is derived from carvenone:



Although the above result renders it probable that terpinene nitronitrosite has the same carbon arrangement in respect of the position of the double linkings, as terpinene, and that therefore during the treatment with nitric acid a migration of the double linking from Δ^4 to Δ^3 has not taken place, this does not settle the question whether the very small quantity of carvenone oxime from the nitrosite must not be considered as a product of conversion during the reduction. But it may now be concluded from the formation of carvenone oxime, that in the terpinene molecule a double linking is in the Δ^1 position. It would be a matter of interest to try whether a hydrocarbon can be produced from carvenone which is identic with terpinene.

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[1]) Liebig's Annalen **343** (1905), 28.
[2]) Berl Berichte **38** (1905), 2730.
[3]) Berl. Berichte **38** (1905), 2022; Report October **1905**, 100.

J. Houben[1]) reports on syntheses of aromatic carboxylic acids by means of Grignard's reaction. It is a well known fact that, according to V. Grignard, carboxylic acids can readily be obtained by allowing carbon dioxide to act on the organomagnesium salts, and decomposing the intermediate products formed with dilute sulphuric acid: $R \cdot MgX + CO_2 = R \cdot CO \cdot OMgX$; $R \cdot COOMgX + H_2O = R \cdot COOH + HO \cdot MgX$.

Already in 1902, J. Houben and L. Kesselkaul[2]) have employed this method for the production of aromatic and hydroaromatic carboxylic acids. The work under review gives the composition of a few syntheses in the series of aromatic and hydroaromatic carboxylic acids. First of all Houben describes the action of magnesium and p-dibrombenzene in ethereal solution in the presence of a small quantity of methyl iodide. By allowing carbon dioxide to act on the reaction mass, he obtained terephthalic acid in addition to p-brombenzoic acid and p-dibrom-acetophenone.

Hydropinene carboxylic acid $C_{10}H_{17} \cdot COOH$, he obtained in a yield of about 40%, by pouring on 14 gm. magnesium in about 100 cc. absolute ether, a concentrated ethereal solution of 100 gm. solid pinene hydrochloride $C_{10}H_{17}Cl$, to which a small quantity methyl iodide has been added. After several days, dry carbon dioxide is introduced into the reaction mass. Next, the mass is decomposed with ice and dilute mineral acid, and from the ethereal layer the acid is isolated with soda solution. Hydropinene carboxylic acid boils at atmospheric pressure at 268°, at 13 mm. pressure at 153°; melting point 72 to 74°. It is a monobasic acid of the formula $C_{11}H_{18}O_2$.

The corresponding anhydride (hydropinene carboxylic acid anhydride $C_{22}H_{34}O_3$) is formed fairly quantitatively when the acid is boiled for half an hour with ten times the weight of acetyl chloride. It crystallises from alcohol in silky brilliant feathers of the melting point 211 to 212°.

Hydrodicamphene. $C_{10}H_{17} \cdot C_{10}H_{17}$, is formed by the action of magnesium on pinene hydrochloride in ethereal solution, according to Wurtz's synthesis, in a yield of 19 to 22%, when 2 molecules pinene hydrochloride act on 1 molecule magnesium with formation of magnesium chloride and hydrodicamphene. It crystallises from alcohol in feathery crystals of the melting point 74 to 75° and boiling point 322 to 323°. It is scarcely attacked by concentrated sulphuric acid and by chromic acid. At 12 mm. pressure it distils at 180° to 190° as a water-white liquid, and appears to be identical with the hydrocarbon $C_{20}H_{34}$, produced by A. Etard and G. Meker[3]), and also by

[1]) Berl. Berichte **38** (1905), 3796.
[2]) Berl. Berichte **35** (1902), 2519 and 3695.
[3]) Compt. rend. **126** 1898), 525.

Letts[1]), from pinene hydrochloride and sodium, and whose melting point the above-mentioned authors indicated as 75°, boiling point 326 to 327°.

Borneol is also formed, in a yield of about 20%, when magnesium is allowed to act on pinene hydrochloride. It is present, in addition to hydrodicamphene, in the ethereal layer of the reaction mass, and distils over in the first fractions. It was produced in the pure state by esterification of the corresponding fractions with phthalic acid anhydride. Borneol owes its origin clearly to the action of the oxygen of the air on hydropinene magnesium chloride, when in all probability borneolate is formed.

By the action of magnesium and carbon dioxide on bornyl chloride $C_{10}H_{17}Cl$, an acid of the melting point 72° is formed, bornyl carboxylic acid $C_{10}H_{17}COOH$, which is identical in every respect with hydropinene carboxylic acid.

Alcohols.

When reducing carvacrol according to the method of Sabatier and Senderens[2]), L. Brunel[3]) obtained two isomeric alcohols of the formula $C_{10}H_{20}O$. The compounds, designated as α- and β-carvacromenthols, have the following properties:

α-Carvacromenthol is an oily, colourless liquid with the odour of safrol and thyme oil. The boiling point lies at 219°.

β-Carvacromenthol could be purified by its phthalic acid compound, which could be recrystallised from alcohol; it is an oily, colourless liquid with a pleasant odour reminding of safrol and peppermint. Boiling point 222°; d_0 0,918. Of this alcohol the following derivatives were produced; 1. β-carvacromenthyl formate, from formic acid and the alcohol; boiling point 229° d_0 0,954. — 2. β-carvacromenthyl acetate, from acetic acid and the alcohol at 130°; boiling point 231,5°; d_0 0,933. — 3. The acid succinic ester from succinic anhydride and the alcohol; melting point 74°. — 4. The acid phthalic ester from phthalic anhydride and the alcohol; melting point 136°.

Menthol. J. Kondakow[4]) enters into theoretical considerations on the subject of the five stereo-isomeric menthols hitherto known. He mentions first the ordinary l-menthol, whose properties and derivatives have hitherto been examined most in detail. It is well known that in the production of these derivatives, both stereo-

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[1]) Berl. Berichte **13** (1880), 793.
[2]) Comp. Report October **1905**, 100—105.
[3]) Compt. rend. **141** (1905), 1245.
[4]) Journ. f. prakt. Chem. II. **72** (1905), 185.

chemical and chemical isomerisations occur, so that the final products no longer correspond to secondary, but to tertiary menthol. But in Kondakow's opinion, the assumption of an intermediary formation of d-menthol does not yet explain this fact satisfactorily. A more recent examination of d-menthol which Kondakow[1]) had produced by reduction from the ketone contained in oil of buchu leaves, has, namely, shown that this body, contrary to the opinion held up to the present, is not by any means unstable. Its haloid anhydrides are all dextrorotatory. In producing them, isomerisations take place — as in the case of l-menthol —, and there occur consequently stable, dextrorotatory, genuine derivatives of d-menthol, as well as unstable derivatives belonging to the tertiary menthol. Menthene, obtained from l-menthol, is dextrorotatory. Different from Kondakow's d-menthol is the isomenthol of Beckmann[2]), which is formed jointly with d-menthol, when either l- or d-menthone is reduced.

Isomenthol is dextrorotatory, and differs from d-menthol by a higher melting point (83,5 to 84°) and a lower specific rotatory power ($[\alpha]_D$ + 25,64° to 27,07°). On oxidation it is converted into d-menthone[3]), which forms a dextrorotatory oxime. Although a more detailed examination of isomenthol and its derivatives is still wanting, it may be concluded, in view of its optical behaviour, that in respect of the stereochemical configuration of its molecule, it occupies an intermediary position between the two first menthols, with an approach towards d-menthol. Another l-isomenthol which would approximate more towards the l-antipode is not yet known, but can possibly be produced by means of reduction from iso-l-menthone. There are further known three inactive menthols. One of these was obtained by Kremers[4]) from optically inactive menthone. It melts at 29 to 31°, and may possibly be identical with the β-thymomenthol of the melting point 27° and boiling point 217° obtained by Brunel[5]) from thymol. The second was produced by Beckmann[6]). Baer[7]) found a third liquid inactive menthol, which, however, according to its physical properties and chemical behaviour, stands closer to the terti-

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[1]) Journ. f. prakt. Chemie II. **63** (1901), 49; Report April **1901**, 14.

[2]) Journ. f. prakt. Chemie II. **55** (1897), 14; Report April **1897**, 53.

[3]) According to tests by Skworzow, d-menthone ($[\alpha]_D$ + 26,91°), when treated with ammonium formate, also yields formyl-d-menthylamine of the m. p. 117 to 118° $[\alpha]_D$ + 154,47°, with little l-amine.

[4]) Amer. chem. Journ. **18** (1896) 762; Report October **1896**, 54.

[5]) Compt. rend. **140** (1905), 252; **137** (1903), 1268; Bull. Soc. Chim. III. **33** (1905), 269; **34** (1905), 500; **35** (1905), 569; Report April **1905**, 103; October **1905**, 103.

[6]) Journ. f. prakt. Chem. II. **55** (1897), 30; Report April **1897**, 53.

[7]) On the synthesis of an inactive menthene. Thesis, Leipzig **1898**; Report October **1898**, 56.

ary menthol which is now also produced by synthesis. With carbanil it forms no urethane, but loses readily thereby water, and yields an inactive menthene. Schindelmeiser has recently examined tertiary menthol more closely in Kondakow's laboratory, and has found that it behaves like Baer's alcohol. The menthene formed in the same manner has the following constants: boiling point 170 to 175°; $d_{4°}^{20°}$ 0,812; $n_{D20°}$ 1,45627; $\alpha_D \pm 0°$. It forms a liquid nitrosochloride which passes over undecomposed with water vapour, which does not readily split off hydrochloric acid with sodium alcoholate or alcoholic potash, and consequently does not readily yield nitrosomenthene. The nitrosochloride boils at 128 to 140° (11 mm. pressure), and is inactive. The solid nitrosochloride from Kremers' menthol cannot be driven over with water vapour without decomposition. Kondakow has obtained another inactive menthol, different from Baer's, when reducing diosphenol; boiling point 214,5 to 216° (atmospheric pressure), 98 to 100,5° (12 mm. pressure), $d_{20°}$ 0,9052, n_D 1,464456, molecular refraction 47,59. It congeals on cooling, and with suitable treatment yields an inactive menthene of the following properties; boiling point 168 to 169°, $d_{4°}^{19,8°}$ 0,8264, molecular refraction 45,73. This menthol greatly resembles Brunel's[1]) α-thymomenthol, for which the following constants are given: boiling point 215,5°; $d_{0°}$ 0,913; melting point — 5°. The corresponding menthene boils at 167 to 168°, $d_{15°}$ 0,823. But whether these two menthols are identical must remain for the present an open question.

With regard to the examination of the oil of buchu leaves, Kondakow states further that dipentene and limonene are present in it. The ketone to which reference has already been made, boils at 86° (10 mm. pressure); α_D — 51°. It forms a liquid oxime and a hydrazone of the melting point 80°, further two semicarbazones with the melting points 180 and 123°. From the former is regenerated by means of sulphuric acid a strongly inverted ketone with the following physical constants: boiling point 85,5 to 86° (10 mm. pressure), $d_{19,5°}$ 0,897, $[\alpha]_D$ — 22,3°, n_D 1,45169, molecular refraction 46,28.

Tertiary menthol, and from it an inactive menthene, have been produced by W. H. Perkin jun.[2]) by synthesis in the following manner: α-Bromohexahydro-p-toluylic acid, formed from hexahydro-p-toluylic acid on treatment with phosphorus pentachloride and bromine, yields on hydrolysis with dilute soda solution, in addition to Δ_1-tetrahydro-p-toluylic acid, α-hydroxyhexahydro-p-toluylic acid of the melting

[1]) Bull. Soc. Chim. III. **33** (1905), 569; Report April **1905**, 103.
[2]) Proceed. Chem. Soc. **21** (1905), 255.

point 132°. The last-named acid is readily converted under the action of dilute sulphuric acid into 1,4-methycyclohexanone of the boiling point 170°. The reaction takes place with elimination of carbonic oxide. At the same time, considerable quantities of Δ_1-tetrahydro-p-toluylic acid are formed. With magnesium isopropyliodide the ketone forms tertiary menthol of the boiling point 95° (25 mm. pressure). The alcohol, when heated with potassium bisulphate, splits off water, and is converted into inactive menthene of the boiling point 168°. The nitrosochloride of this menthene is solid, and like that of the menthene obtained by Kremers and Urban[1]), melts at 128°.

Sesquiterpene alcohols. Eyken[2]) reports on the occurrence of sesquiterpene alcohols in the distillates of a few aromatic woods of the Malay Archipelago.

Some considerable time ago van Romburgh had obtained by steam distillation from the "Kajoe garoe" (fragrant wood) of Macassar, whose botanical origin was unknown, an oil interspersed with solid crystals, which Eyken examined more closely. By expressing and purifying the crystals, they were recognised by their melting point 93°, by analysis, optical rotation $[\alpha]_D - 30°$, and molecular refraction, as guaiol; a comparison with guaiol from guaiac wood oil confirmed the identity. In the liquid portions of the oil free acids were found, chiefly formic and acetic acids. Subsequently Eyken himself produced the oil by distilling the wood; the latter he suspected to be a conifer, possibly a species of juniper. He obtained the oil in a yield of 1,3 %; it soon became solid, but, contrary to the oil first examined, it contained no fractions passing over below the boiling point of guaiol; the fractions boiling higher than guaiol remained also liquid, and thereby rendered it more difficult to work out the latter, which should therefore be obtained not by fractionating, but by freezing out. In spite of the differences Eyken considers the two oils to be identical, and attributed the variations to this, that the one oil had been stored for several years, the other one being a fresh distillate.

The same author obtained a sesquiterpene alcohol differing from those known up to the present, in the course of an examination of the oil of *Gonostylus Miquelianus* T. et B., the wood of which also has the name "Kajoe garoe". This oil was also solid, and melted towards 66° to 68°; boiling point 280° to 290°; $[\alpha]_D$ in absolute alcohol $+ 35°$. In order to remove resins, the oil in ethereal solution was washed with potash liquor, and after evaporating the ether, distilled twice. When

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[1]) Amer. chem. Journ. **16** (1894), 385; Report April **1894**, 72.

[2]) Receuil des trav. chim. des P.-B. **25** (1906), 40, 44. Chem. Centralbl. **1906**, I, 841.

distilled with water vapour, however, the colourless oil decomposed, and yielded a distillate with an acid reaction and a solid resin-like residue. For this reason, the solid body of this oil must be obtained by freezing out; after recrystallisation from acetic acid and from alcohol it showed the following constants: formula $C_{25}H_{26}O$, melting point 82°; boiling point 164 to 166° (17 mm. pressure), molecular weight calculated 222, found 232, 228, $[\alpha]_D$ in absolute alcohol + 30°. Eyken gives it the name "gonostylol". When boiled with formic acid the alcohol was converted into a sesquiterpene $C_{15}H_{24}$, gonostylene, of the boiling point 137° to 139° (17 mm.) $d_{17°}$ 0,9183, $[\alpha]_D$ in absolute alcohol + 40°, molecular refraction found 66,7 calculated for $C_{15}H_{24}O$ 66,15. It is remarkable that guaiol and guaiene have the same rotatory power, but in the reverse direction. With hydrochloric acid and with bromine respectively only oily products of addition were obtained. When treated with glacial acetic and sulphuric acids according to Bertram-Walbaum, no alcohol was formed; the bulk of the terpene remained unchanged.

Aldehydes and ketones.

We have already repeatedly discussed in our Reports the method for the determination of aldehydes and ketones with neutral solution of sodium sulphite, recommended by Sadtler[1]), and have in every case been compelled to question the accuracy of this method, as an exact titration of the solution containing sodium sulphite is not possible. Further studies of his method have shown Sadtler[2]) that he was in error with regard to the increase in the application of his method. The author determined again the usefulness of the method for citral, cinnamic aldehyde, benzaldehyde, vanillin, carvone, pulegone, formaldehyde, citronellal, camphor, menthone and fenchone. Of these compounds, citral, cinnamic aldehyde, carvone, pulegone, and formaldehyde reacted with 2 molecules sodium sulphite; benzaldehyde and vanillin with 1 molecule sodium sulphite, and the others not at all.

In almost every case Sadtler now lets the liquid with oil and neutral sulphite stand overnight, in order to be sure that no further alkali is formed. Previous to adding the sulphite solution, the oils are neutralised with $^1/_{10}$th normal alkali solution. Sadtler has recently stated that the disappearance of the characteristic odour (especially in citral, cinnamic aldehyde, carvone, pulegone, and benzaldehyde) is an important sign of the end of the reaction.

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[1]) Report April **1904**, 48; October **1904**, 119; April **1905**, 103; October **1905**, 30.

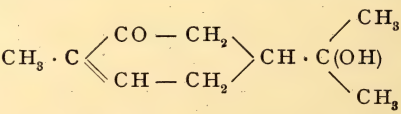
[2]) According to reprint from the Journ. Americ. Chem. Soc. **27** (1905), 1321.

The author concludes from the results obtained, that the presence of double linkings and their situation towards the CHO-or CO-group, and also of the benzene nucleus and its situation, have an influence on the reaction between neutral sodium sulphite and aldehydes and ketones. As formaldehyde reacts so very readily, the reaction appears to occur all the more easily, the smaller the molecular weight is of the body which enters into reaction. In Sadtler's opinion the CHO-group specially appears to become active in this reaction, and not the double linking, as Tiemann believes. Salicylic aldehyde, anisic aldehyde, cuminic aldehyde and heliotropin also appear, like benzaldehyde, to react only with 1 molecule neutral sodium sulphite.

After experiments[1]) which we have recently made again, we are unable to alter anything in our previously expressed opinion on Sadtler's method; its usefulness for exact determinations fails on account of the impossibility of titrating the sodium sulphite solution exactly.

Benzaldehyde. With regard to the determination of small quantities of benzaldehyde according to Hérissey, see page 107 of the present Report.

Carvone. Knoevenagel and Samel[2]) have obtained in a round-about way the oxydihydrocarvone produced by Rupe and Schlochoff[3]), by bringing carvone in solution by boiling with alkali bisulphite liquor, and letting this solution stand together with strong acids at ordinary temperature. In supersaturating with soda liquor, 80% of the carvone were then separated off as carvone hydrate (as the authors call this body). It is formed, as in the case of Rupe and Schlochoff's method, by attaching water to the double linking of the side-chain of carvone. Carvone hydrate



has the following properties: boiling point 160° at 16 mm. pressure, melting point 42 to 43° (from ligroin and petroleum ether), $[\alpha]_{D\,20°} + 43°$ in 25,85 per cent. alcoholic solution. It is insoluble in water (according to Rupe and Schlochoff it is readily soluble); phenylhydrazone, melting point 134 to 135°; oxime, 112,5 to 114°; semicarbazone, 177

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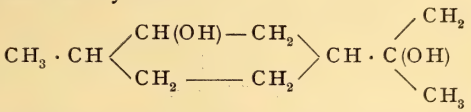
[1]) Compare the present Report, p. 70 and 74.
[2]) Berl. Berichte **39** (1906), 677.
[3]) Berl. Berichte **38** (1905), 1719. Report October **1905**, 112.

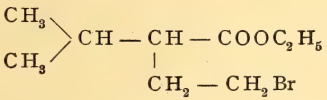
to 179°. When heated *in vacuo* for a prolonged time, carvone hydrate is converted in carvacrol and carvone; when heated for one hour with potassium bisulphate to 170°, it yields quantitatively carvacrol. The hydroxyl-group could not be detected either with benzoyl chloride or with phenyl isothiocyanate; all efforts to condense carvone hydrate with benzaldehyde also failed. Reduction with sodium and alcohol led to dihydrocarveol hydrate



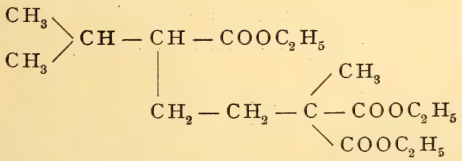
melting point 112°; $[\alpha]_{D20°} + 19{,}2°$ in 24,74 per cent. alcoholic solution. Reduction with zinc dust and potash liquor, carried out in a manner analogous to the reduction of carvone to dihydrocarvone, yielded dihydrocarvone hydrate of the boiling point 138 to 139° (9 mm. pressure); $d\frac{19°}{4°}$ 1,006; $n_{D20°}$ 1,476; $[\alpha]_{D20°} - 18{,}5°$ in 18,48 per cent. alcoholic solution; semicarbazone melting point 150,5° to 151°. Dihydrocarveol hydrate could be oxidised with chromic acid and glacial acetic acid to dihydrocarvone hydrate.

Camphor. Dihydrocamphoric acid, formed when camphoric acid and potash are melted together, is, according to Martine, α-methyl-α-isopropyladipic acid, which is also obtained on oxidation of benzylidene menthone. In order to confirm this formula, G. Blanc[1]) has made an attempt to arrive at this acid by synthesis.

He reduced for this purpose isopropylsuccinic acid, according to a method[2]) already described previously, with sodium in absolute alcohol. The α- and β-isopropyl-butyrolactones were treated with phosphorus pentabromide and subsequently with alcohol. Thereby is formed the ester

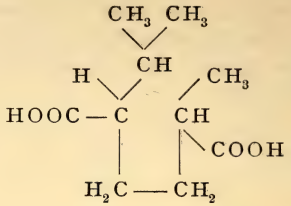


which is converted with sodium methyl malonic acid ester, with formation of



[1]) Compt. rend. **141** (1905), 1030.
[2]) Compt. rend. **139** (1904), 203.

This ester yields on saponification an acid melting at 158°, which on being melted splits off carbonic acid, and is converted into α-methyl-α-isopropyladipic acid:

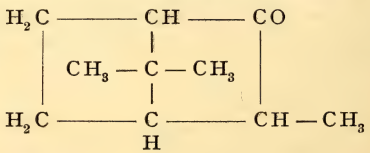


It melts at 103°, and corresponds to dihydrocamphoric acid. But the latter is optically active, whilst the synthetic acid is inactive.

In continuation of a work on the electrolytic reduction of the imide of camphoric acid[1]) which has led to the formation of the so-called camphidones and of camphidine, J. Tafel and H. Bublitz[2]) publish the result of their investigations which deal with the elucidation of the constitution of these reduction products.

Camphocarbonic acid, as is well known, splits up, when heated, into carbon dioxide, and camphor. W. Balcom[3]) has investigated the physical progress of this reaction. We content ourselves with a reference to this work.

Fenchone. On the strength of recent investigations, F. W. Semmler[4]) has convinced himself that the formula



drawn up by Wallach[5]) for fenchone, and up to the present recognised as correct, does not agree with all the facts. If it is accepted with Kondakow, that in the formation of fenchyl chloride from fenchyl alcohol a transposition takes place into the tertiary fenchyl chloride, in which the chlorine atom and the methyl-group are linked

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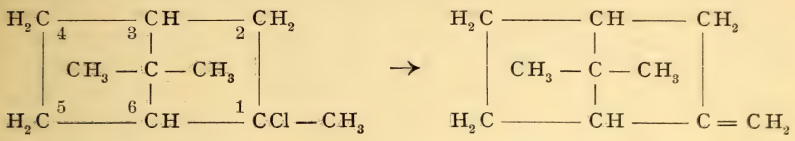
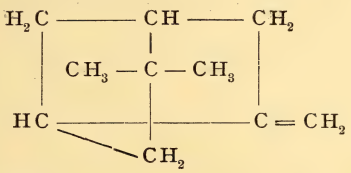
[1]) Berl. Berichte **34** (1901), 3274.
[2]) Berl. Berichte **38** (1905), 3806.
[3]) The chemical kinetics of the loss of carbon dioxide from camphocarbonic acid. Thesis, Heidelberg, **1905**.
[4]) Chem. Ztg. **29** (1905), 1313.
[5]) Liebig's Annalen **300** (1898), 319.

to the same carbon-atom, there may originate, with loss of hydrochloric acid, on the one hand a fenchene of the formula I, "camphor fenchene", but on the other hand there might be formed with ring-disruption between the carbon atoms 1 and 6, a fenchene of the formula II, "isofenchone fenchene": —



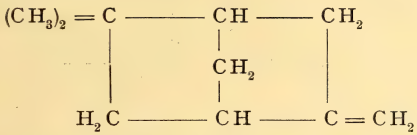
Fenchyl chloride I. Camphor fenchene

and

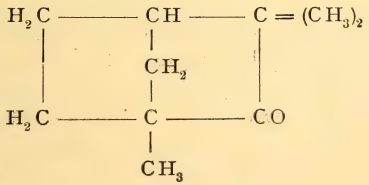


II. Isofenchone fenchene

Formula II is identical with



It this is accepted, the formation of the two semi-cyclic fenchenes from Wallach's fenchone formula could be explained. But according to more recent investigations by Semmler, this hypothesis cannot be sustained without further proof. Particularly by the results of the oxidation in alkaline and neutral solutions, which led from fenchone to isocamphoronic acid and dimethyl tricarballylic acid, Semmler was induced to draw up the following formula for fenchone: —

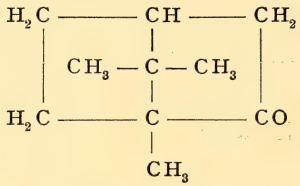


The formation of the two acids could be explained from this formula without re-arrangement. Gardner and Cockburn[1]) also ob-

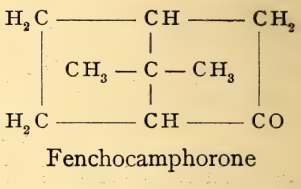
[1]) Journ. Chem. Soc. **73** (1898), 708.

tained the above acids from fenchone, but with concentrated nitric acid, whilst Wallach had had already before him dimethyl malonic acid, formed by further oxidation of dimethyl tricarballylic acid. The conversion of fenchone into m-cymene, discovered by Wallach, would also be intelligible in accordance with Semmler's fenchone formula; similarly, the relationship existing between camphor and fenchone, and also the various well-known reactions of fenchone and its derivatives, would find a better explanation by the new formula. In agreement with the new formula are further the physical properties of fenchone, and this is particularly evident if the properties of camphor and fenchone are contrasted.

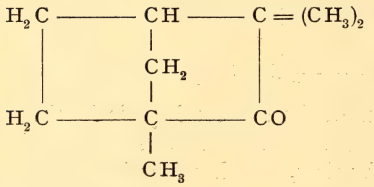
According to this, camphor and fenchocamphorone on the one side, and fenchone and camphenilone on the other, go together.



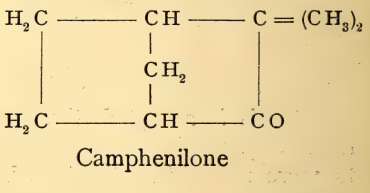
Camphor



Fenchocamphorone



Fenchone



Camphenilone

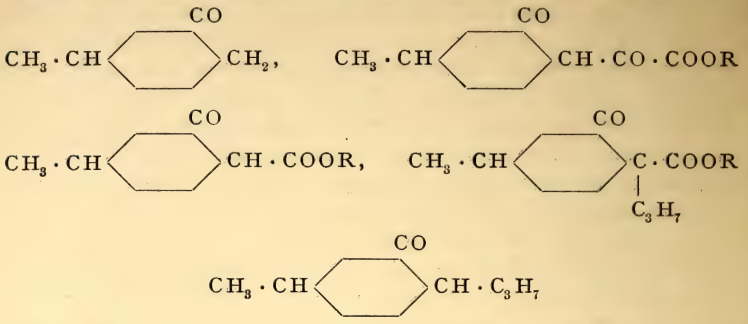
Camphor would consequently be methylated fenchocamphorone, and fenchone methylated camphenilone.

Menthone. A. Kötz and L. Hesse[1]) report on a synthesis of menthone from methylhexanone. They condense methylhexanone and ethyl oxalate by adding a strongly cooled mixture of ester and ketone in small portions to a solution of sodium ethylate which is kept cold. The temperature may thereby rise only slightly and temporarily above that of the freezing mixture. After standing for 15 hours, the dark-brown reaction mixture is introduced into very dilute sulphuric acid of 0°; the oxalic ester of methylhexanone formed

[2]) Liebig's Annalen **342** (1905), 306.

is abstracted from the aqueous liquid by repeatedly extracting with ether. It is clear from the following results of this work that the oxalic acid ester enters the methylhexanone in para-position towards the methyl-group, and that consequently methyl-1-hexanone-3-oxalic ester-4 has been formed. The condensation-product gives a dark-brown coloration in alcoholic solution with ferric chloride. Concentrated soda liquor splits up the ester into methyl hexanone and sodium oxalate. With ammonia it also reproduces the ketone and oxamide. The crude condensation product yields with copper acetate a bright green copper salt, which melts at 153°. The pure ester separated from the copper salt by dilute sulphuric acid boils at 163° (12 to 13 mm. pressure); $d_{15°}$ 1,0903. Its semicarbazone melts above 245°. Dilute sulphuric acid or soda liquor saponify it readily into methylhexanone oxalic acid which melts at 132°. When heated with aniline in a water bath, the ester forms a pyrrolidone derivative of the formula $C_{21}H_{20}ON_2$. When distilled at atmospheric pressure, it is converted with loss of carbonic oxide into methyl-1-hexanone-3-carboxylic ester-4, a mobile liquid of the boiling point 128,5° (15 mm. pressure); $d_{14°}$ 1,057. Its copper salt melts at 155°. With phenylhydrazine the ester yields a pyrazolone of the melting point 243° to 245°; with ammonia tetrahydromethyl anthranilic acid ester of the melting point 67°. The corresponding methyl ester stands, according to the odour, in no relation whatever to methyl ester of methyl anthranilic acid. With suitable treatment with methyl iodide and a solution of sodium in methyl alcohol, methyl-hexanone carboxylic ester is converted into methyl-1-hexanone-3-methyl-4-carboxylic ester-4. The specific gravity of the ester boiling at 120° to 122° (12 mm. pressure) is 1,0189 (19°). The isopropyl ester constituted in an analogous manner boils at 135° to 137° (10 mm. pressure); $d_{14°} = 1{,}009$. Its semicarbazone melts at 144° to 145°. When splitting up the ketone with concentrated methylalcoholic potash there is formed the natural d-menthone of the boiling point 206° to 208°; $d_{18°}$ 0,898; $[\alpha]_D + 11{,}68°$; the corresponding semicarbazone melts at 184 to 185°. As in this case the specific rotatory power ($[\alpha]_D + 28{,}14°$) is only about half as large as that of the d-menthone which can be obtained from natural l-menthone by inversion with concentrated sulphuric acid, it may be assumed that in the case before us, lævorotatory menthone is present in addition to a preponderance of dextrorotatory menthone. On reduction with sodium and alcohol, only lævorotatory menthone is formed, of which one fraction boils at 214° to 216°, and congeals into crystals melting at 37°. The other fraction of the boiling point 212° to 214° can only be obtained crystallised by continued cooling. The urethanes of both menthols melt at 111°, like that of natural menthol. The formation of the ordinary para-menthone has proved that the above condensation product

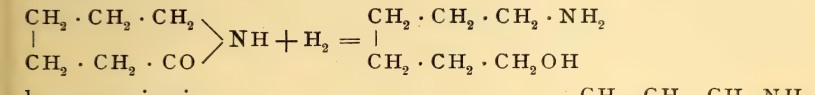
and the bodies which can be derived from it possess the accepted formula, which finds expression in the following diagrams: —



Methylheptenone. In connection with a short theoretical contemplation of the base $C_8H_{15}N$ [1]) which he had previously obtained from methyl heptenylamine and described, O. Wallach [2]) reports on a new base $C_8H_{16}:NH$, isomeric with coniine, which had been produced from the same crude material. It is formed, besides a hydrocarbon C_8H_{14}, by the addition of hydrogen chloride or hydrogen bromide to methylheptenyl amine, and subsequent dry distillation of the addition product. The base has the following properties: boiling point 150 to 151°; d 0,823; $n_{D20°}$ 1,4398; melting point of the hydrochloride 218 to 220°, of the chloroplatinate 221 to 233°. It yields a quaternary iodide of the composition $C_8H_{16}N(CH_3)_2I$ (melting point 242 to 243°), a nitroso compound and a sulphone amide of the melting point 76 to 78°. The constitutional formula of the base is probably

$$(CH_3)_2 \cdot CH \cdot CH \cdot CH_2 \cdot CH_2$$
$$\quad\quad\quad

point 134 to 138°; d 0,863; n_{D24} 1,4575; melting point of the hydrochloride 203 to 204°, of the benzoyl compound 149°, the urea 195 to 196°) could be separated off. The hexamethylenimine which might be expected could not be isolated. As only pure isoxime free from oxime was used, the occurrence of cyclohexylamine can only be explained by ring-disruption and new ring-formation in the following manner: —

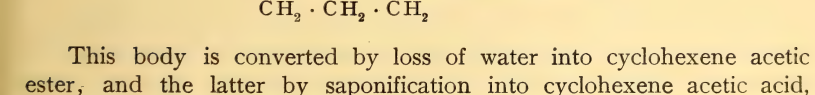


hexanone isoxime

cyclohexylamine.

Wallach mentions further the conditions under which the nitrosochloride of cyclohexene (tetrahydrobenzene) which had already been obtained in small quantity by Baeyer, is produced in a better yield. It has not yet been possible to convert this nitrosochloride in the still unknown oxime of hexenone.

In an analogous manner to methyl cyclohexanone[1]), Wallach obtained by the action of bromoacetic ester on cyclohexanone in the presence of zinc or magnesium, cyclohexanol acetic ester: —



This body is converted by loss of water into cyclohexene acetic ester, and the latter by saponification into cyclohexene acetic acid, which melts at 37 to 38°, and boils at 140° at 12 mm. pressure. By adding bromine it yields a brominated acid (melting point 119 to 120°), and on oxidation with potassium permanganate in a weak alkaline solution, an oil with a hexanone-like odour, whose semicarbazone melts at 203 to 204°. The analysis points to a compound with seven carbon atoms, which, however, possesses the character of an aldehyde.

Acetylcyclohexanone. George Leser[2]) has obtained by condensation of cyclohexanone and acetic ester by means of sodium, in a fairly good yield, acetylcyclohexanone, a liquid with a penetrating odour, which boils at 111 to 112° at 18 mm. pressure; $d_{0°}$ 1,0782; n_D 1,51384.

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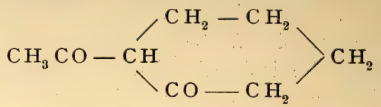
[1]) Liebig's Annalen **314** (1900), 151. Report April **1901**, 61.
[2]) Compt. rend. **141** (1905), 1032.

Acetylcyclohexanone

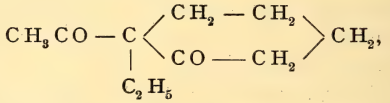


forms a monosemicarbazone of the melting point 159°, and a dioxime. It dissolves readily in alkalies. When the alkaline solution is heated, a complete hydrolytic decomposition occurs, and if hydrochloric acid is added, acetylcaproic acid separates off: —

$$CH_3CO-CH_2-CH_2-CH_2-CH_2-CH_2-COOH.$$

This boils at 184 to 185° at 15 mm. pressure, and congeals into a mass melting at 30°. On oxidation with bromine and soda liquor it is converted into normal pimelic acid of the melting point 103°.

Acetylcyclohexanone has a mobile hydrogen atom which can be replaced by radicals. Leser for example obtained the ethyl derivative



which, however, no longer shows the characteristic properties of the β-diketones. The study of these derivatives is continued.

Phenols and phenol ethers.

Béhal and Tiffeneau[1]) have continued their earlier investigations[2]) of phenol ethers with ψ-allyl side-chain $-C(CH_3):CH_2$, and, starting from the three o-, m-, and p-substituted ψ-anethols, ψ-allyl-p-phenetol, ψ-safrol, and ψ-methyleugenol, they have arrived at the following results. On reduction with sodium and alcohol, the ψ-allyl group is reduced to isopropyl; thus, in the case of isopropylphenetol, the OC_2H_5-group was eliminated by hydriodic acid, and the free phenol identified by its melting point and that of its benzoate. If the ψ-allyl bodies are oxidised with aqueous chameleon solution in the cold, there are formed, with loss of CO_2, substituted acetophenones: —

$$R\cdot C(CH_3):CH_2 \xrightarrow{O} R\cdot CO\cdot CH_3 + CO_2.$$

When hypoiodous acid is added, iodohydrins $R\cdot C(OH)(CH_3)\cdot CH_2I$ are formed, which behave differently when hydriodic acid is split off, according to the reagent employed. If they are treated in

[1]) Compt. rend. **141** (1905), 596.
[2]) Compt. rend. **139** (1905), 139.

ethereal solution with potash powder, there are formed intermediarily, by substitution of the iodine atom by OH and loss of water, oxides

$$R \cdot C(CH_3) \cdot CH_2$$
$$\diagdown O \diagup$$

which on distillation at atmospheric pressure converted into are hydratropic aldehydes $R \cdot CH(CH_3) \cdot CHO$. But if the hydriodic acid is split off with silver nitrate or mercuric oxide, there occurs, as already previously observed, a very remarkable migration of the carbon linkings, with formation of β-ketones, that is to say, formation of a normal side-chain:

$$R \cdot C(OH)(CH_3) \cdot CH_2I \xrightarrow{-HI} R \cdot CH_2 \cdot CO \cdot CH_3.$$

In this manner were produced from ψ-anethol β-anise ketone, from ψ-allyl phenetol p-ethoxy phenyl acetone, from ψ-safrol methylene dioxyphenyl acetone, and from ψ-methyl eugenol dimethoxyphenyl acetone, and the two last-named were identified by means of the semicarbazones with the products obtained in another way by Wallach and by Hoering.

According to Fourneau and Tiffeneau[1]) substituted ethylene oxides of the benzene series behave differently, according to the position of the substitute when they are rearranged by the application of heat. The authors differentiate between monosubstituted oxides

$$R \cdot CH_2 \cdot CH \cdot CH_2,$$
$$\diagdown O \diagup$$

symmetricallyl disubstituted

$$R \cdot CH \cdot CH \cdot CH_3,$$
$$\diagdown O \diagup$$

and asymmetrically disubstituted oxides

$$R \cdot C(CH_3) \cdot CH_2$$
$$\diagdown O \diagup$$

The first-named oxides, such as the oxides derived from allylbenzene, estragol, safrol, and methyl eugenol, which pass over without decomposition at reduced pressure, are converted by distillation at ordinary pressure in substituted hydrocinnamic aldehydes, $R \cdot CH_2 \cdot CH_2 \cdot CHO$, which were identified by the melting points of their semicarbazones.

The symmetrically disubstituted oxides are converted into β-ketones of the formula $R \cdot CH_2 \cdot CO \cdot CH_3$; there was, for instance, obtained from phenyl propenyl oxide

$$C_6H_5 \cdot CH \cdot CH \cdot CH_3$$
$$\diagdown O \diagup$$

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[1]) Compt. rend. **141** (1905), 662. Comp. ibid. **140** (1905), 545. Report October **1905**, 118.

phenyl acetone (boiling point 214—215°, melting point of the semicarbazone 198°); in an analogous manner from anethol oxide, the anethol ketone (Tardy's anise ketone) obtained also by Hoering[1]).

The asymmetrically disubstituted oxides, as will be seen from the above report, are converted into substituted hydratropic aldehydes, which had already been produced by Bougault[2]) in an entirely different manner.

In all these conversions, there occur no molecular migrations (transposition of carbon linkings).

In our Report of October **1904**, 11, we communicated the results of a work by Hoering, according to which, in the treatment of monobromo anethol bromide $CH_3O \cdot C_6H_3Br \cdot CHBr \cdot CHBr \cdot CH_3$ with nitric acid, the bromine atom of the side-chain in the α-position enters the benzene ring, with formation of a ketone $CH_3O \cdot C_6H_2Br_2 \cdot CO \cdot CHBr \cdot CH_3$. This peculiar atomic transposition was recently also observed by Hoering in the anethol dibromide itself, when even with moderate oxidation with nitric, chromic, or glacial acetic acid, a ketone $CH_3O \cdot C_6H_3Br \cdot CO \cdot CHBr \cdot CH_3$ is formed in a good yield. An examination of the secondary products formed shows that there also occur secondary products non-brominated in the nucleus; on the other hand, when the latter are oxidised, higher brominated products are formed, *e. g.*, dibromo anisic acid. In order to solve the problem whether this entrance of bromine in the nucleus must not be attributed to the occurrence of free bromine, numerous oxidation experiments were made, especially with dilute solution of potassium permanganate. But as, in spite of every precaution, this examination did not lead to any definite result, Hoering endeavoured to come to a decision in an indirect way, by oxidising α-methoxy-β-bromo-dihydrobromo anethol $CH_3O \cdot C_6H_3Br \cdot CH(OCH_3)CHBr \cdot CH_3$. He found that with moderate oxidation of this body, no further bromine atom enters the benzene ring, as almost exclusively the ketone $CH_3O \cdot C_6H_3Br \cdot CO \cdot CHBr \cdot CH_3$ was formed.

On oxidising isosafrol dibromide, the author did not succeed in arriving at a separation of the secondary products; on the other hand, when the dibromide was treated with a mixture of nitric and glacial acetic acids, it was converted into an acetyl derivative $CH_2O_2 \cdot C_6H_2(NO_2) \cdot CH(OCOCH_3)CHBr \cdot CH_3$, nitrated in the nucleus,

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[1]) Berl. Berichte **38** (1905), 2296. Report October **1905**, 117; compare also the following abstracts.

[2]) Annal. de Chim. et Phys. VII. **25** (1902), 515, 549, 560. Report April **1903**, 11.

which with alcoholic potash yielded a propylene oxide $R \cdot CH \overset{O}{\diagdown\diagup} CH \cdot CH_3$. This conversion established the position of the two bromine atoms in the side-chain, and confirmed the accuracy of the pseudo-formula accepted by Hoering for the reactive dibromides.

The facility with which the bromine atom in the α-position of the dibromides of propenyl phenol ethers is exchanged, was followed up some time ago by Pond[1]) and Hell[2]). Hoering[3]) has again investigated this reactivity in anethol, isosafrol, and the corresponding derivatives brominated in the nucleus, in order to determine whether the entry of bromine in the benzene nucleus influences the mobility of the bromine atom in α-position of the side chain. He thereby found that as a rule these dibromides brominated in the nucleus, if the reaction lasts sufficiently long, lead to the analogous bodies as the dibromides themselves. There were produced in the usual manner substitution and also addition products of the general form

$$R \cdot CH(OCH_3) \cdot CHBr \cdot CH_3,$$
$$R \cdot CH(OH) \cdot CHBr \cdot CH_3,$$
$$R \cdot CH(OCOCH_3) \cdot CHBr \cdot CH_3,$$
$$R \cdot C(OCH_3) : CH \cdot CH_3,$$
$$R \cdot CH : CBr \cdot CH_3,$$
$$R \cdot C \vdots C \cdot CH_3.$$

In the same measure as the reactivity of the α-bromine atom diminishes with the entry of bromine in the benzene nucleus, the capacity of the β-bromine atom of splitting off decreases. The β-bromine atom in the acetates $R \cdot CH(OCOCH_3) \cdot CHBr \cdot CH_3$, for instance, can only be replaced by acetoxyl with formation of monoacetates $R \cdot CH(OH) \cdot CH(OCOCH_3) \cdot CH_3$.

The compounds $R \cdot CH(OH) \cdot CHBr \cdot CH_3$ and $R \cdot CH(OCOCH_3) \cdot CHBr \cdot CH_3$, which are derived from the dibromides, are, as Hoering published in a preliminary communication[4]), very readily converted, by boiling with alcoholic potash, in substituted propenyl oxides of the formula $R \cdot CH \overset{O}{\diagdown\diagup} CH \cdot CH_3$. In a more detailed publication[5]) Hoering has continued the study of these oxides, preferably with the oxides derived from mono- and dibromoisosafrol dibromides, as these were suitable for the purpose on account of their crystallisation capacity.

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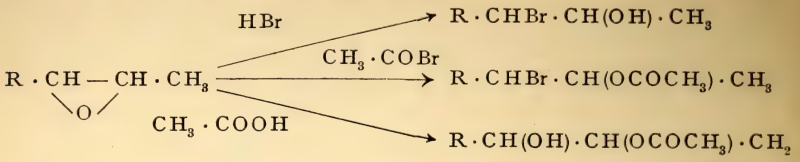
[1]) Journ. Amer. chem. Soc. **25** (1905), 292. Report October **1903**, 98.
[2]) Berl. Berichte **36** (1903), 1184. Report October **1903**, 98.
[3]) Berl. Berichte **38** (1905), 3464.
[4]) Berl. Beriehte **38** (1905), 2296. Report October **1905**, 117.
[5]) Berl. Berichte **38** (1905), 3477.

Like the ethylene oxides, these oxides also readily attach atom-groups according to the following formulæ:



The oxide oxygen atom therefore always remains linked to the β-carbon atom, as is also the case in converting the oxides by heating or treatment with acids into β-ketones $R \cdot CH_2 \cdot CO \cdot CH_3$. The bromine atom of the side-chain in the α-position, in the addition products of the oxides, is, as might be expected, very mobile; in fact in the α-bromo-β-oxy compounds so much so, that they decompose with evolution of hydrogen bromide.

With regard to the very rich experimental matter of these works, we must refer to the original treatises.

Nitrogenous bodies.

The conversion of aldehydes and ketones into bases by boiling with ammonium formate, has first been accomplished by Leuckart. He obtained the formyl compounds of the primary, secondary and tertiary bases corresponding to the crude material. O. Wallach has applied this reaction already a long time ago to terpene ketones. The occurrence of the mixture of bases and of the formyl compounds as final products complicated the production of the bases in the pure state, and for this reason Wallach[1]) set himself the task of removing this defect in the reaction. If the formyl compounds were only formed as secondary products from a primarily formed base and formic acid, a lowering of the temperature should prevent the formation of these compounds. This has in many cases proved to be feasible, and has at the same time identified the formyl compounds as secondary products of the reaction. The progress of the reaction could now be explained as is expressed in the following formulæ: —

1. $R_2CO + NH_3 = R_2C\begin{matrix}OH\\NH_2\end{matrix}$

2. $R_2C\begin{matrix}OH\\NH_2\end{matrix} + HCOOH = R_2C\begin{matrix}H\\NH_2\end{matrix} + CO_2 + H_2O,$

in which formic acid represents the reducing agent. If then the primary base has an opportunity of entering in reaction with a still

[1]) Liebig's Annalen **343** (1905), 54.

unchanged ketone or aldehyde, it will be possible that, besides primary, secondary and even tertiary bases are also formed, as the following example with benzaldehyde shows: —

I. $C_6H_5COH + NH_3 = C_6H_5CH\begin{matrix}OH\\NH_2\end{matrix} \rightarrow C_6H_5CH_2NH_2$

II. $C_6H_5COH + NH_2CH_2C_6H_5 = C_6H_5CH\begin{matrix}OH\\NH\cdot CH_2C_6H_5\end{matrix} \rightarrow (C_6H_5CH_2)_2NH$

III. $C_6H_5COH + NH(CH_2C_6H_5)_2 = C_6H_5CH\begin{matrix}OH\\N(CH_2C_6H_5)_2\end{matrix} \rightarrow (C_6H_5CH_2)_3N.$

This explains Leuckart's observations. Wallach further argues that if the base is withdrawn from the reaction-mixture by adding a suitable free acid, the uniform progress of the reaction will be promoted, inasmuch as only primary, or (when salts of the primary base are sufficiently dissociated at the existing temperature) only secondary, or further also only tertiary base will be formed. The hypothesis of the progress of the reaction further permits of the possibility of bringing besides ammonia, substituted primary or secondary bases in the pres-, ence of free formic acid so into reaction with aldehydes and ketones, that new substituted bases are formed. The experiment has confirmed the hypothesis, and has given the following results: —

1. The reaction can be accomplished practically uniformly by adding free anhydrous formic acid or acetic acid.

2. It is possible to keep the temperature of the conversion mostly fairly low, and as a consequence the final products obtained are mainly the salts of the bases formed. Only in a few cases, especially with aromatic bases and with menthone, the occurrence of the formyl compound cannot be prevented.

3. The sphere of application is very large owing to the fact that different aldehydes and ketones can be brought into reaction with different bases.

In the experimental part of Wallach's work, a number of such bases produced by the above-mentioned reaction are described: —

Diethylcarbinamine $(C_2H_5)_2CH\cdot NH_2$ from diethyl ketone, ammonium formate, and acetic acid at 165°; boiling point 90°.

α-Phenylethylamine $C_6H_5CH(NH_2)CH_3$ from acetophenone, ammonium formate, and acetic acid, at 155°; boiling point 186°;

melting point of the hydrochloride 160°. The formyl compound is formed without adding acetic acid. Boiling point 200° at 14 mm. pressure.

Cyclodihexylamine $NH(C_6H_{11})_2$ from cyclohexanone, ammonium formate, and acetic acid at 120° to 130°; boiling point 251 to 252°, d 0,925; $n_{D18°}$ 1,4861; nitrosamine, melting point 105 to 106°.

Benzylcyclohexylamine $NH\begin{cases} CH_2C_6H_5 \\ C_6H_{11} \end{cases}$ from cyclohexanone, benzylamine, and formic acid, at 150°; b. p. 281 to 282°.

Dicyclomethylhexylamine $NH(C_6H_{10}CH_3)_2$ from methyl hexanone, ammonium formate, and formic acid at 120 to 130°, boiling point 134 to 135° at 12 to 14 mm. pressure, at atmospheric pressure in a current of hydrogen 273°; d 0,8878; $n_{D21°}$ 1,4756.

The base is a mixture of stereo-isomeric compounds. The same mixture was also, in conformity with the theory, obtained from methylcyclohexanone, methylcyclohexylamine, and formic acid at 150°.

Amylmethylcyclohexylamine $NH\begin{cases} C_5H_{11} \\ C_6H_{10}\cdot CH_3 \end{cases}$ from amylamine, methylhexanone, and formic acid at 150°; boiling point 234°;

Benzylmethylcyclohexylamine $NH\begin{cases} CH_2C_6H_5 \\ C_6H_{10}\cdot CH_3 \end{cases}$ from benzylamine, methylhexanone, and formic acid at 150°; boiling point 165 to 170° at 12 mm. pressure; d 0,946; $n_{D22°}$ 1,5182. The same base was also obtained from benzaldehyde, methylcyclohexylamine formate, and formic acid, at 160°.

Formylmenthylamine $C_{10}H_{19}NH\cdot CHO$ from menthone, ammonium formate, and glacial acetic acid, at 175 to 185°. The temperature of conversion is so high in this case, that the formyl compound is formed from the formate produced primarily.

Triisoamylamine $(C_5H_{11})_3N$ from valeric aldehyde, ammonium formate, and formic acid, at 90 to 130°; boiling point 265 to 270°.

Tribenzylamine $(C_6H_5CH_2)_3N$, from benzaldehyde, ammonium formate and formic acid at 135°; melting point 91°.

Diamylaniline $(C_5H_{11})_2N\cdot C_6H_5$ from valeric aldehyde, aniline formate, and formic acid at 70 to 100°, and then 105 to 110°; boiling point 264 to 265°.

Methylamylaniline $(CH_3)(C_5H_{11})N\cdot C_6H_5$ from valeric aldehyde, methyl aniline and formic acid at 110°.

Benzylaniline $C_6H_5CH_2NH \cdot C_6H_5$ from benzaldehyde, aniline formate, and formic acid at 120 to 125°, melting point 32°. The reaction with formation of secondary products does not proceed quite evenly.

Ethylbenzylamine $(C_2H_5)(CH_2C_6H_5) \cdot NH$ from benzaldehyde, ethylamine hydrochloride, sodium formate, and formic acid at 150°; boiling point 199°. First of all the formyl compound was formed which could be saponified with hydrochloric acid.

Benzylpiperidine $C_6H_5CH_2 \cdot N \cdot C_5H_{10}$ from piperidine, benzaldehyde, and formic acid at 180°; boiling point 248°.

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